JRC Scientific and Technical Reports

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Interlaboratory Comparison Report

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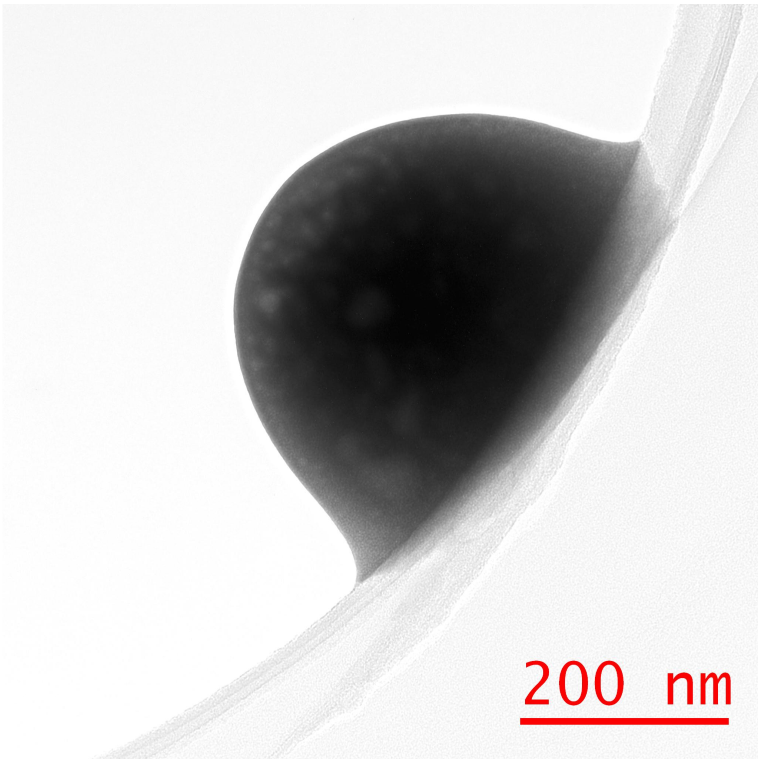

EUR 23702 EN - 2008

EUROPEAN COMMISSION

Institute for Reference Materials and Measurements

The mission of the IRMM is to promote a common and reliable European measurement system in support of EU policies.

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JRC 49869

EUR 23702 EN
ISBN 978-92-79-08378-5
ISSN 1018-5593
DOI 10.2787/18380

Luxembourg: Office for Official Publications of the European Communities

Printed in Belgium

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December 2008

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NUSIMEP

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1 Summary

The Additional Protocol (AP) authorizes safeguards authorities to verify the absence of undeclared nuclear activities in all parts of a state's nuclear fuel cycle as well as any other location where nuclear material is or may be present. As part of the Additional Protocol, environmental sampling has become an important tool for the detection of non-declared nuclear activities. In environmental sampling micrometer-sized uranium particles with an isotopic composition characteristic for the processes at the inspected facility need to be collected, identified and analysed. Considering the potential consequences of the analyses, these measurements need to be subjected to a rigorous quality management system.

NUSIMEP-6 focused on measurements of *Uranium isotope amount ratios in uranium particles* aiming to support laboratories involved in uranium particle analysis. It was the first NUSIMEP on particle analysis coordinated by IRMM and was also intended as a pilot interlaboratory comparison in this field to gather feedback towards future optimisation and improvements. NUSIMEP-6 was open for participation to all laboratories in the field of particle analysis, particularly also to the IAEA network of analytical laboratories for environmental sampling (NWAL).

The NUSIMEP test samples were prepared by controlled hydrolysis of well certified uranium hexafluoride close to natural uranium isotopic composition. Participating laboratories in NUSIMEP-6 received a test sample of uranium particles on a graphite planchet with undisclosed isotope amount ratio values $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$, $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$. The uranium isotope amount ratios were to be measured using their routine analytical procedures. Measurement of the major ratio $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ was obligatory; measurements of the minor ratios $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$ were optional.

15 institutes reported measurement results using different analytical methods, among those were 7 NWAL laboratories. The participants' measurement results were evaluated against the certified reference values. In addition, zeta scores were calculated.

The results of NUSIMEP-6 confirm the capability of laboratories in measuring the ratio $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ and $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ in uranium particles. Difficulties were particularly observed for the ratio $n(^{236}\mathrm{U})/n(^{238}\mathrm{U})$. In addition feedback from the participants was collected in view of improvements and optimisation of future NUSIMEP interlaboratory comparisons for uranium isotope amount ratios in uranium particles.

2 NUSIMEP

The IRMM Nuclear Signatures Interlaboratory Measurement Evaluation Programme (NUSIMEP) is an external quality control programme organised by the Joint Research Centre - Institute for Reference Materials and Measurements (IRMM). NUSIMEP was established in 1996 to support the growing need to trace and measure the isotopic abundances of elements characteristic for the nuclear fuel cycle present in trace amounts in the environment. Such measurements are required for safeguards applications as well as for the implementation of the Treaty on the Non-Proliferation of Nuclear Weapons (NPT) [1].Measurements of the isotopic ratios of the elements uranium and plutonium in small amounts, such as typically found in environmental samples, are required for nuclear safeguards, for the control of environmental contamination and for the detection of nuclear proliferation.

Laboratories participating in NUSIMEP are requested to measure the parameters specified using their standard methods and invited to report measurement results with uncertainties to IRMM. Those reported measurement results are compared with independent external certified reference values with demonstrated traceability and uncertainty, as evaluated according to international guidelines. Laboratory performance evaluation is according to ISO guidelines on performance evaluation in proficiency testing by interlaboratory comparisons [2].
Laboratories analysing environmental samples are invited to participate in these external NUSIMEP quality control exercises to demonstrate and assess their ability to carry out precise measurements in particular on trace amounts of uranium and plutonium. Through this and similar programmes, the degree of equivalence of measurements of individual laboratories can be ascertained. Reports on previous NUSIMEP interlaboratory comparisons can be found on the IRMM web-site [3].

3 Introduction

Nuclear safeguards arrangements exist on international level under the protocols of the International Atomic Energy Agency (IAEA) [1] on European Union level under the Euratom Treaty [4] and on regional levels. The INFCIRC/540 [5], also referred to as the Additional Protocol (AP) moved the focus from exclusively accounting for known quantities of fissile material towards a more qualitative system that is able to provide a comprehensive picture of a state's nuclear activities. Through unannounced inspections and nuclear material balances, safeguards inspectors are able to verify that no nuclear material is diverted from its intended peaceful use. As part of the Additional Protocol, environmental sampling has become an important tool for the detection of non-declared nuclear activities. Analysis of environmental samples is carried out to detect the (unavoidable) traces in the environment originating from technological activities. One extensively developed technique in environmental sampling (ES) makes use of pieces of cotton cloth called swipes to wipe surfaces inside and around a nuclear facility. The dust collected on these swipes typically contains micrometer-sized uranium particles with an isotopic composition characteristic for the processes at the inspected facility. Measurements of minor isotope abundance ratios of uranium in those particles, may provide additional information about equipment or plant design, indicate information about irradiation history, and also help to evaluate mixing and decay scenarios. Major and minor uranium isotope ratios in environmental samples collected by inspectors are measured by the IAEA's Seibersdorf Analytical Laboratory (SAL) in Austria and the Network of Analytical Laboratories (NWAL) [6].

Recently a workshop organised by the ESARDA Working Group on Standards and Techniques for Destructive Analysis (WG DA) was held at IRMM on measurements of minor isotopes in uranium bulk and particle samples [7]. Participants in this workshop came from the main European and international nuclear safeguards organisations, nuclear measurement laboratories as well as from geochemistry and environmental sciences institutes. During this workshop it was stressed that considering the potential consequences of particle analyses in nuclear safeguards, bio- and earth sciences, these measurements need to be subjected to a rigorous quality management system. The reliability and comparability of measurement results of isotope ratios in uranium particles need to be guaranteed and monitored via the correct use of reference materials and quality tools. Currently it is clearly a significant drawback for laboratories involved in particle analysis that such materials are not available. Therefore special attention has been given recently at IRMM to the development of uranium particle reference materials and quality control samples for the analysis for environmental samples [8, 9].
To address the needs from international safeguards authorities and research institutions IRMM organised the first NUSIMEP interlaboratory comparison on isotope ratio measurements in uranium particles.

4 Scope and aim

Measurements of the isotopic ratios of the elements uranium and plutonium in small amounts, such as typically found in environmental samples, are required for nuclear safeguards, for the control of environmental contamination and for the detection of nuclear proliferation. NUSIMEP-6 aims at laboratories carrying out particle analysis in these various application fields. Particular emphasise was given to participation of the IAEA network of analytical laboratories for environmental sampling (NWAL) in support to nuclear safeguards arrangements. Participation of the NWAL laboratories in this NUSIMEP interlaboratory comparison was formally recommended by the IAEA at the IAEA Technical Meeting on Particle Analysis of Environmental Samples for Safeguards. NUSIMEP-6 is a pilot interlaboratory comparison that not only should picture the measurement capabilities of the participating laboratories at a certain point in time, but also collect feedback from the participants towards future improvements and needs, which made this pilot interlaboratory comparison a very useful exercise for the coordinators as well as for the participating laboratories.

Measurands and matrix
Measurands are the isotope amount ratio values n(^{234}U)/n(^{238}U), n(^{235}U)/n(^{238}U) and n(^{236}U)/n(^{238}U). The matrix is uranium particles on a graphite planchet.

IRMM's international measurement evaluation programmes
Several NUSIMEP interlaboratory comparisons of measurements of uranium isotopic ratios were organised previously: for example NUSIMEP 2, uranium isotopic abundances in dry uranium nitrate samples; NUSIMEP 3, uranium isotopic abundances in saline media and NUSIMEP 4, uranium isotopic abundances in a simulated urine and NUSIMEP 5 uranium, plutonium and caesium isotopic ratios in saline medium [3]
The organisation of the interlaboratory comparison follows the standard procedures of the Interlaboratory Measurement Evaluation Programmes IMEP, REIMEP, NUSIMEP of the Institute for Reference Materials and Measurements (IRMM) of the Joint Research Centre, a Directorate-General of the European Commission. This programme is accredited according to ISO Guide 43-1 [10]. The designation of this interlaboratory comparison is NUSIMEP-6.

5 Time frame

NUSIMEP-6 was announced for participation beginning February 2008. Registration was opened from February to March 2008. After the ESARDA workshop on measurements of minor isotopes in uranium bulk and particle samples held at IRMM 10-11 April three late registrations were accepted in response to workshop participants' requests for participation in NUSIMEP-6. A confirmation of registration was sent to the participants and subsequently the samples were dispatched in May 2008. Reporting deadline was 10 July 2008. This deadline was extended by 5 weeks for participants using Fission Track Thermal Ionisation Mass Spectrometry due to unforeseeable limitations in access to a nuclear reactor. The homogeneity and stability studies were carried out between May and October 2008.
Beginning September the certified reference values were sent to the participants.

6 Test material

6.1 General remarks

The process applied at IRMM to produce uranium particles from well certified uranium uranium hexafluoride (UF_6) is described in detail in [8]. In the meantime an improved aerosol deposition chamber was developed at IRMM to control the relative humidity and temperature during the production of uranium particles from the controlled hydrolysis of uranium hexafluoride (UF_6) aiming at the production of single uranium particles in the 1μm range. This new aerosol deposition chamber was used to produce the reference particles for the NUSIMEP-6 interlaboratory comparison.

6.2 Preparation

Preparation of the uranium reference particles

A depleted UF_6 reference material with a $n(^{235}U)/n(^{238}U)$ ratio of 0.0070439(35), stored in a Monel (cupper-nickel alloy) ampoule, was used for NUSIMEP-6. Milligram amounts of this UF_6 reference material was distilled into a glass vial. The set-up of the distillation unit is shown in Fig. 1.

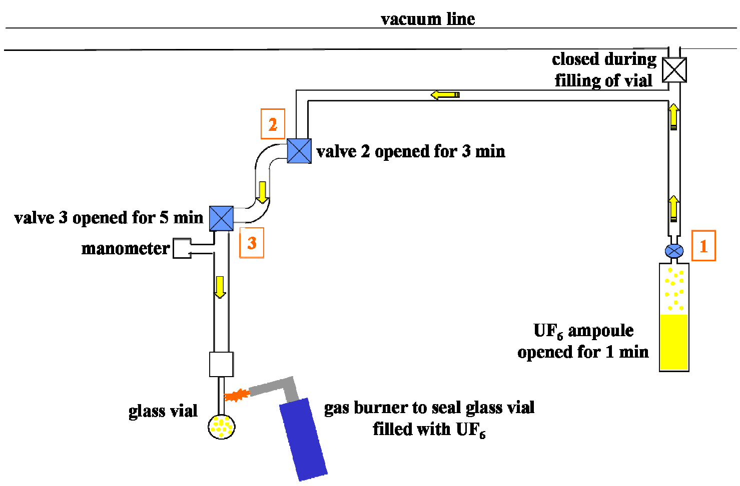

Fig. 1: The distillation unit showing the stepwise procedure to transfer milligram amounts of certified UF_6 from a reference material ampoule to a glass vial

After transfer, the glass vial containing the gaseous UF_6 was placed into the upper part of the aerosol deposition chamber. The apparatus consists of an aluminium cylindrical reaction chamber with lids in Plexiglas (Fig. 2). The glass vial containing the UF_6 reference material was broken by a pin that was inserted by turning a screw from the top of the chamber. In this way, the UF_6 was released and subsequently hydrolyzed.

Fig. 2: Set-up of the aerosol deposition chamber

The humidity and the temperature of the air inside the chamber were monitored by a hygrometer (Rotronic). The relative humidity varied between 51 % and 67 %. The temperature of the air was about 21 ºC. The reaction between the released uranium hexafluoride and the atmospheric moisture in the deposition chamber proceeds very rapidly to form solid uranium oxyfluoride particles and hydrogen fluoride. The simplified overall equation is as follows:

$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$

At the base of the aerosol deposition chamber, a retractable platform containing 6 graphite discs of 25 mm diameter was used to collect the settling uranium oxyfluoride particles. This platform was inserted in the chamber a few seconds after breaking the glass vial. In this way, the collection of glass shards from the UF_6 vial, that are generally much larger than the uranium-bearing particles, was avoided. The uranium oxyfluoride particles were collected for about 4 hours. After this time, the graphite discs could be removed from the aerosol deposition chamber. They were placed into an open furnace at 350 ºC for at least 15 hours, in order to remove excess water and other volatile elements. This heating procedure typically removed most of the fluorine in the particles, hereby changing the molecular structure to U_3O_8. The particle morphology was then verified by scanning electron microscopy (SEM) for all of the NUSIMEP-6 samples.

The NUSIMEP-6 samples were put in boxes with silica-gel and sealed in plastic bags and stored at room temperature until dispatch.

6.3 Verification

The NUSIMEP-6 uranium particles are produced from a well certified uranium hexafluoride reference material. This reference material was certified in the chemical form of uranium hexafluoride by gas mass spectrometry for the $n(^{235}U)/n(^{238}U)$ ratio and in the form of uranium nitrate by thermal ionisation mass spectrometry for the $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ ratios. From previous studies it was known that no isotopic effects occur during aerosol deposition of uranium hexafluoride [[8]]. Nevertheless, measurements on blank planchets and on samples taken from each badge produced were performed using thermal ionisation mass spectrometry (TIMS). A drop of nitric acid was put onto a blank planchet and after a certain time allowing for any possible particles to dissolve taken up with a pipette. Subsequently this drop was transferred onto carburized rhenium filaments to increase the ionisation efficiency [[11], [12]]. The TIMS measurements were performed using the "multiple ion counting" (MIC) system of the TRITON TIMS, operated in multi-dynamic mode, as described in [[13]]. The method repeatability required was 0.2% for $n(^{235}U)/n(^{238}U)$ and to 3% for $n(^{234}U)/n(^{238}U)$. Due to the extremely small $n(^{236}U)/n(^{238}U)$ ratio in this test material the method repeatability for TIMS analysis was expected between 10%-70% for measurements.

6.4 Homogeneity

Due to the limited number of test samples (6 planchets) that can be produced per deposition in the aerosol deposition chamber the strategy was adopted for the homogeneity study measuring one planchet for the isotopic composition of uranium per batch produced. 5 series of 6 planchets were prepared using the aerosol deposition chamber. All planchets were investigated using scanning electron microscopy (SEM) to check the particle density and subsequently measured according to the procedure described in paragraph 6.3. Results from all these measurements were evaluated by a one-way analysis of variance ANOVA [14, 15, 16]. This allows the separation of the method variation (s_{wb}) from the experimental averages over one unit to obtain estimation for the real variation between units (s_{bb}). The measurement variation sets a lower limit u^*_{bb} to the between unit variance which depends on the mean squares between units, the number of replicate measurements per unit and the degrees of freedom of the mean squares between units. The uncertainty of homogeneity is consequently estimated as s_{bb} or in case of $s_{bb}<u^*_{bb}$ as u^*_{bb}. The variation between units (s_{bb} or u^*_{bb}, respectively) for $n(^{234}U)/n(^{238}U)$ was 0.82% and for $n(^{235}U)/n(^{238}U)$ 0.04%. Measurements of the $n(^{236}U)/n(^{238}U)$ were close to detection limit and the counting statistics for the signals were extremely low. Therefore only 4 measurement results were available and the u^*_{bb} was around 67%, which is still acceptable for the purpose of this ILC. This approach, applying single factor ANOVA analysis as described in [14, 15, 16] was found to be comparable to tests to determine whether an ILC material is sufficiently homogeneous for its purpose as described in ISO 13528[2]. Essentially, these tests compare the between units heterogeneity with the standard deviation for proficiency assessment $\hat{\sigma}$. Assessment criterion for a homogeneity check is s_{bb} (or u^*_{bb}) $\leq 0.3\hat{\sigma}$. One aim of the pilot NUSIMEP-6 ILC is to picture the present measurement capabilities for uranium particle analysis. Results from NUSIMEP-6 can serve as a valuable input to safeguards authorities to define assessment criteria for the future, particularly for the minor isotopes. The present safeguards requirement for the measurement as presented recently at the ESARDA workshop on measurements of minor isotopes in uranium bulk and particle samples can be translated into a $\hat{\sigma}$ of about 1% for the $n(^{235}U)/n(^{238}U)$ ratio in uranium particles [7]. There are no official requirements concerning the measurement performance for the minor ratios of uranium for the time being. The only safeguards requirement is that in case the isotope amount fraction of the minor isotopes is above 1ppm, NWAL laboratories have to be able to measure the respective isotope amount ratio; for isotope amount fractions below 1ppm an upper limit has to be reported to the safeguards authorities. Therefore to assess the homogeneity the standard deviation for proficiency assessment $\hat{\sigma}$ was set to $0.01X_{ref}$ for $n(^{235}U)/n(^{238}U)$, $0.05X_{ref}$ for $n(^{234}U)/n(^{238}U)$ and X_{ref} for $n(^{236}U)/n(^{238}U)$ according to methods proposed in ISO 13528.
The tests indicate that the uranium test material is sufficiently homogeneous for all the ratios in the frame of this ILC, see Table 1.

6.5 Stability

From previous interlaboratory comparison and production of isotopic reference materials it is well known that no isotopic effects occur over time when storing samples properly. Therefore after the homogeneity was assessed to be fit for purpose the sample dispatch was started. Nevertheless a short term stability study was carried out with the aim to verify the isotope ratios on one planchet with an isochronous setup at 2 temperatures (room temperature and 60 °C). The planchet was kept at 60 °C for a period of 4 weeks and then measured after 6 months, at a time when all the participants had already reported their measurement results. Methods to assess whether an ILC material is sufficiently stable for its purpose are described in ISO 13528 [2]. Essentially, these tests compare the general averages of the measurand obtained in the homogeneity check (x_s) with those obtained in the stability check (y_s). The absolute difference of these averages is again compared to the standard deviation for proficiency assessment $\hat{\sigma}$. Assessment criterion for a stability check is $|x_s-y_s| \leq 0.3\hat{\sigma}$.

The tests indicated that the uranium test material is sufficiently stable for all the ratios in the frame of this ILC, see Table 1.

Table 1: Homogeneity and stability test for the uranium isotope amount ratios according to ISO 13528 [2]

	s_{bb} or u^*_{bb}, respectively	standard deviation for proficiency assessment $\hat{\sigma}$	$0.3\hat{\sigma}$	Homogeneity check s_{bb} or u^*_{bb}, $\leq 0.3\hat{\sigma}$	Stability check (4 weeks at 60°C) $\lvert x_s-y_s \rvert \leq 0.3\hat{\sigma}$
$n(^{234}U)/n(^{238}U)$	0.82%	$0.05X_{ref}$	$7.42\cdot10^{-7}$	YES	YES
$n(^{235}U)/n(^{238}U)$	0.04%*	$0.01X_{ref}$	$2.11\cdot10^{-5}$	YES	YES
$n(^{236}U)/n(^{238}U)$	67%*	X_{ref}	$1.5\cdot10^{-7}$	YES	YES

This is the relative maximum heterogeneity that could be hidden by method repeatability (u_{bb}). It is larger than (and therefore replaces) the relative between units standard deviation s_{bb}.

It was recommended to the participants to store the sample in a dry environment after receipt.

6.6 Distribution

The ILC samples were dispatched to the participants by IRMM on 5-6 May 2008. Each participant received a package with one graphite planchet, a letter with information on particle density, sample handling, result reporting and a form to confirm receipt of the package.

7 Participant invitation, registration and information

Participation of the NWAL laboratories in this NUSIMEP interlaboratory comparison was formally recommended by the IAEA at the IAEA Technical Meeting on Particle Analysis of Environmental Samples for Safeguards. Furthermore NUSIMEP-6 was announced in relevant conferences and meetings. Invitations were sent to the NWAL laboratories and other participants who expressed interest in participation. Measurement of the major ratio $n(^{235}U)/n(^{238}U)$ was obligatory measurements of the minor ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ were optional. Participants were invited to follow their routine procedures.
Participants were also informed that their measurement results will be evaluated against the certified reference values, on the confidentiality of results and the fee of € 100 for participation. The call for participation was also released on the IRMM website and confirmation of registration was sent to those participants who had registered (cf. annex 1 and annex 2). This confirmation contained further details on the envisaged time frame. Instructions on measurands, sample storage, and measurement were sent to the participants together with the samples. The instructions also contained the individual code for access to the result reporting and related questionnaire website (cf. annex 3, annex 4). After closure of the result reporting the participants received the NUSIMEP-6 reference values. Table 2 lists the number of participants per country.

Table 2: Participants per country

Country	**Number of participants**
United Kingdom	5
Russian Federation	1
United States	3
Japan	3
China	1
France	2
Germany	1
Austria	2
Italy	1
Hungary	1

8 NUSIMEP-6 Reference values

The NUSIMEP-6 uranium particles are produced from a well certified uranium hexafluoride reference material. This reference material was certified in the chemical form of uranium hexafluoride by gas mass spectrometry and in the form of uranium nitrate by thermal ionisation mass spectrometry. The certificate is attached in annex 8.

Table 3 lists the NUSIMEP-6 reference values X_{ref} and their associated standard uncertainties u_{ref} and expanded uncertainties U_{ref} (k=2).

Table 3: NUSIMEP-6 reference values

Isotope Amount Ratio	**Certified Value**	**Expanded Uncertainty *U*, *k*=2**
$n(^{234}U)/n(^{238}U)$	0.000 049 817	0.000 000 048
$n(^{235}U)/n(^{238}U)$	0.007 043 9	0.000 003 5
$n(^{236}U)/n(^{238}U)$	0.000 000 520 48	0.000 000 000 86

9 Reported results

9.1 General observations

Fifteen institutes reported measurement results, among those 7 NWAL laboratories. Participants from the same institute applying more than one analytical method had to register separately. All 20 registered participants submitted results in NUSIMEP-6 and completed the associated questionnaire. The laboratories were asked to apply their routine measurement procedure and to report only one result on the isotope ratios as deduced from their replicate measurements with uncertainty and coverage factor. All laboratories reported results for the major ratio $n(^{235}U)/n(^{238}U)$, one of those laboratories reported only an upper limit rather than the isotope amount ratio. 14 participants reported results for the minor ratio $n(^{234}U)/n(^{238}U)$ and only 6 participants reported a measurement result for the $n(^{236}U)/n(^{238}U)$ ratio, another 6 reported an upper limit for the same ratio. One participant reported results for the uranium isotope ratios that were a factor 10-100000 higher than expected. All results in NUSIMEP-6 are displayed/listed uncorrected as reported by the participants.

Table 4: Reported results per participant

Country	$n(^{234}U)/n(^{238}U)$	$n(^{235}U)/n(^{238}U)$	$n(^{236}U)/n(^{238}U)$
Austria	✓	✓	✓
Austria	✓	✓	✓
China		✓	
France		✓	
France	✓	✓	✓
Germany	✓	✓	✓
Hungary		✓	✓
Italy	✓	✓	✓
Japan	✓	✓	
Japan	✓	✓	
Japan	✓	✓	✓????
Russian Federation	✓	✓	
United Kingdom		✓	
United Kingdom	✓	✓	✓
United Kingdom	✓	✓	✓
United Kingdom	✓	✓	✓
United Kingdom	✓	✓	✓
United States		✓	
United States		✓	
United States	✓	✓	✓

9.2 Measurement results

Annexes 5-7 list the individual measurement results and display overview graphs. The graphs for $n(^{234}U)/n(^{238}U)$ and $n(^{235}U)/n(^{238}U)$ show a roughly normal distribution with no irregularities. In case of $n(^{236}U)/n(^{238}U)$ only 4 participants reported results within +/- 100% deviation from the reference value. The other participants reported ratios that were too large or reported an upper limit for $n(^{236}U)/n(^{238}U)$. According to safeguards requirements NWAL laboratories can report an upper limit in case the isotope amount fraction of the minor isotopes is below 1ppm, which is the case in NUSIMEP-6; $n(^{236}U)/n(U)$ < 1ppm (see also paragraph 10.1).

Annexes 5-7 also display the results from the NWAL laboratories and results according to participant's replies to the questionnaire.

10 Scoring of results

10.1 The scores and their settings

Individual laboratory performance is expressed in terms of z and zeta scores in accordance with ISO 13528 [2]:

$$z = \frac{x_{lab} - X_{ref}}{\hat{\sigma}} \qquad \text{and} \qquad zeta = \frac{x_{lab} - X_{ref}}{\sqrt{u_{ref}^2 + u_{lab}^2}}$$

Where

x_{lab} is the measurement result reported by a participant

X_{ref} is the certified reference value (assigned value)

u_{ref} is the standard uncertainty of the reference value

u_{lab} is the standard uncertainty reported by a participant

$\hat{\sigma}$ is the standard deviation for proficiency assessment

Both scores can be interpreted as: satisfactory result for |score|≤2, questionable result for 2<|score|≤3 and unsatisfactory result for |score|>3.

z score

The NUSIMEP-6 z score indicates whether a laboratory is able to perform the measurement in accordance with what can be considered as good practice for NWAL laboratories. The standard deviation for proficiency assessment $\hat{\sigma}$ is accordingly based on present safeguards requirements for the measurements of $n(^{235}U)/n(^{238}U)$ in environmental samples and on ILC organiser's assessment after discussions with experts from SAL in the field for the $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ ratios. The IUPAC International Harmonised Protocol [17] suggests that participants can apply their own scoring settings and recalculate the scores if the purpose of their measurements is different. In this ILC, $\hat{\sigma}$ is $0.01X_{ref}$ for $n(^{235}U)/n(^{238}U)$, $0.05X_{ref}$ for $n(^{234}U)/n(^{238}U)$ and X_{ref} for $n(^{236}U)/n(^{238}U)$.

zeta score

The zeta score provides an indication of whether the estimate of uncertainty is consistent with the laboratory's deviation from the reference value [2]. It is calculated only for those results that were accompanied by an uncertainty statement. The interpretation is similar to the interpretation of the z score. An unsatisfactory zeta score may be caused by an underestimated uncertainty or by a large deviation from the reference value.

The standard uncertainty of the laboratory (u_{lab}) was calculated as follows. If an uncertainty was reported, it was divided by the coverage factor k. If no coverage factor was provided, the reported uncertainty was considered as the half-width of a rectangular distribution. The reported uncertainty was then divided by √3, in accordance with recommendations issued by Eurachem and CITAC [18].

10.2 Scoring the reported measurement results

A z score was calculated for all participants except for those who reported no value or an upper limit, "<" value. A zeta score was calculated for results that were accompanied by an uncertainty statement. Annexes 5-7 list the scores per ratio and participant in detail, and annex 11 summarises the scores per participant.

Table 5 summarises the scores per isotope amount ratio.

A large share of participants reported satisfactory measurement results for the $n(^{235}U)/n(^{238}U)$ and $n(^{234}U)/n(^{238}U)$ isotope amount ratios, and only a small share unsatisfactory results. It can be concluded that the participants performed quite well in NUSIMEP-6. For the small $n(^{236}U)/n(^{238}U)$ isotope amount ratio only 2 participants had satisfactory z and zeta scores.

Table 5: Overview of scores: S(atisfactory), Q(uestionable), U(nsatisfactory)

	z score				zeta score				both z and zeta scores
	S	Q	U	n (*)	S	Q	U	n (*)	S
$n(^{234}U)/n(^{238}U)$	86%	-	14%	14	86%	-	14%	14	12
$n(^{235}U)/n(^{238}U)$	74%	16%	10%	19	80%	5%	15%	19	13
$n(^{236}U)/n(^{238}U)$	67%	-	33%	6	50%	-	50%	6	2

(*) n is the number of results for which a score was given.
The total number of participants (with and without a score) is 20.

11 Further information extracted from the results

In addition to submission of the results, the participants were asked to answer a number of questions relating to the measurements. All participants completed the questionnaire. Issues that may be relevant to the outcome of the intercomparison are discussed below.

11.1 Methods of analysis

The methods of analysis applied were TIMS by 3 participants, SIMS by 10 participants, ICP-MS by 5 participants, and alpha spectrometry by 2 participants. 2 participants selected the particle with fission track, the others used either SIMS for particle selection or SEM-EDX. 8 participants involved a particle transfer step prior to measurements by using a vacuum impactor, rubber ball, micro manipulator, collodion film, and by swiping and subsequent heptane extraction. For the $n(^{235}U)/n(^{238}U)$ and $n(^{234}U)/n(^{238}U)$ isotope amount ratios satisfactory measurement results were reported by participants with all the different analytical methods, except for alpha spectrometry. For the $n(^{236}U)/n(^{238}U)$ isotope amount ratio satisfactory measurement results were reported by participants using SIMS and MC-ICP-MS. There were sometimes large differences in the reported uncertainties even among participants using the same instrumental technique. Annex 9 summarise the information given by the participants on instrument parameters and measurement conditions for SIMS, TIMS and LA-ICP-MS.

11.1.1 Correction for mass fractionation / mass bias

75% of the participants applied a correction for mass fractionation / mass bias to their measurement results. Most of the participants used a natural uranium standard to apply a correction to their measurement results.

11.2 A representative study

14 of the 20 participants indicated that the measurements were carried out according to the same analytical procedure routinely used for this kind of samples. 13 participants indicated that they are experienced for this type of measurement. Half of the participants indicated to analyse at least 11-50 samples per year, 5 participants analyse more than 50 samples per year. The mission of half of the laboratories participating in NUSIMEP-6 is to carry out measurements for fissile material control or safeguards but also for environmental sciences, including the 7 NWAL laboratories. The other participants are from the fields of occupational health, research & development, geosciences, material analysis. All but 2 participants indicated that their laboratories are either accredited and/or authorised for this type of measurements. This suggests that NUSIMEP-6 is a useful and representative study for the current capability of laboratories in the field of uranium particle analysis.

11.3 Quality system and use of standards

All laboratories but two indicated that they are working according to a quality management system, mostly according to ISO 17025 and ISO 9000 [19]. 75% of the participants confirmed participation in interlaboratory comparisons. The ILC schemes listed were REIMEP, NUSIMEP, CETAMA, CCQM, CCRI and IAEA ILCs [3, 20, 21, 22]. All participants routinely use certified reference materials mostly for instrument calibration but also for method validation. The certified reference materials used by the NUSIMEP-6 participants are listed in Annex 10.

11.4 Determination of uncertainty

All of the participants who reported results for ratios and not upper limits provided an uncertainty estimate with a coverage factor. All the participants stated that they routinely report uncertainties on chemical measurements to their customers. Half of the participants stated that their reported uncertainties in NUSIMEP-6 are calculated according to the Guides for Quantifying Measurement Uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or EURACHEM/CITAC (2000) [18, 23]. The other half of the participants indicated that they evaluated their measurement uncertainty either via replicate measurements only, which causes that they are likely to underestimate their uncertainty by not taking into account other sources of uncertainty, or via replicate measurements of sample and measurement standards, mass bias correction and correction for isobaric effects, which comes close to a complete uncertainty budget.

11.5 Future NUSIMEP ILCs on particles

NUSIMEP-6 is a pilot interlaboratory comparison that not only should picture the measurement capabilities of the participating laboratories in uranium particle analysis, but also collect feedback from the participants towards future improvements and needs. Participants expressed interest in future NUSIMEP ILCs on particles, particularly on uranium, plutonium and uranium/plutonium mixed samples. A few also expressed the need for neptunium and thorium samples. The feedback on the particle density for future NUSIMEP samples was somewhat depending on the instrumental technique applied, but ranged from a particle density like the present NUSIMEP-6 sample to a smaller particle density for SIMS analysis to a higher particle density for ICP-MS analysis. The isotopic composition of future NUSIMEP particles ranged from depleted uranium, to natural to low enriched to a mixed sample with variable enrichment with a few particles at high enrichment. The majority of the participants also confirmed that they would like to analyse uranium oxyfluoride particles in a future NUSIMEP ILC.

12 Feedback

The questionnaire invited laboratories to provide feedback of any kind to the ILC coordinators. 2 participants would have preferred that the planchet was fixed in the plastic box. Most of the participants also mentioned that particles in the sample were less than 1μm, with only very few up to 5μm, which made particle analysis difficult, particularly for the minor isotopes. It was also suggested to use monodispersed particles for SIMS analysis. The planchets were too heavily loaded for FT-TIMS measurements and too small. Some participants requested a more explicit measurement protocol from the ILC organisers, including the possibility to report results for individual particles. Furthermore streaks and smears of uranium were present on some planchets. This likely occurred during sample deposition. One participant also noted the presence of an isobaric at mass 237 that affected their ability to derive meaningful results for $n(^{236}U)/n(^{238}U)$.

13 Conclusion

There is an increased need for information in order to verify not only the amounts of nuclear material, but also the consistency of information as provided by states or plant operators. To this end, techniques like particle analysis have been implemented. The fundamental importance of measurements of major and minor uranium isotopes in environmental sampling (ES) was recently also stressed by the IAEA during the Workshop on Measurements of Minor Isotopes in Uranium Organized by the ESARDA Working Group on Standards and Techniques for Destructive Analysis (WG DA). The minor uranium ratios are measured in almost all of the environmental samples [7]. The major and minor isotope amount ratios in uranium were the measurands under investigation in NUSIMEP-6. The measurement capabilities in uranium particles for $n(^{235}U)/n(^{238}U)$ and $n(^{234}U)/n(^{238}U)$ were very good, particularly for the NWAL laboratories. Only a few results were reported for the small $n(^{236}U)/n(^{238}U)$ isotope amount ratio. Differences are observed in the uncertainty estimates provided by the participants, even when using same instrumental techniques. At present there are no safeguard requirements on the uncertainties of measurements in particle analysis. The concept of "Target Values for Uncertainty Components" for element and isotope assay of nuclear materials was originally conceived in 1979 by the Working Group on Techniques and Standards for Destructive Analysis (WGDA) of the European Safeguards Research and Development Association (ESARDA) and matured gradually during many years [24]. The definition of performance standards for measurements in particle analysis appears highly recommended. The ESARDA WG DA undertakes establishing such performance standards as guidance for measurement laboratories [25].

The aim of the first Nuclear Signatures Inter-laboratory Measurement Evaluation Programme was to study the capability of analytical laboratories to measure uranium isotope amount ratios in uranium particles. NUSIMEP-6 was intended as a pilot study on uranium particle analysis. One objective of NUSIMEP-6 was also to collect feedback from the participants in view of optimisation of uranium reference particle production. From the feedback it became clear that the parameters for uranium particles produced via aerosol deposition of well characterised UF_6 standards still needs some improvement in view of controlling the particle density, particle size and avoiding additional uranium films on the planchets. The identified needs for reference particles in future NUSIMEP ILCs are manifold. For safeguards analysis a sample with uranium of different enrichment and/or uranium mixed with a few plutonium particles would be required. The analysis of 2 different samples, one with monodispersed particles in combination with "close to real-life" particles produced via aerosol deposition would be beneficial for NWAL laboratories using SIMS, furthermore also the analysis of uranium oxyfluoride particles.

The Safeguards Analytical Laboratory (SAL) particularly acknowledged that NUSIMEP-6 was a very good exercise for SAL, the NWAL laboratories and other experts in this field.

The safeguards analytical laboratory faces more and more challenges in the field of environmental sampling and is in need of reference particles of both uranium and plutonium for instrument calibration, quality control and interlaboratory comparisons with an isotopic composition representative for the range of particles found in nuclear installations.

Acknowledgements

Authors would like to thank Roger Wellum, formerly IRMM, Magnus Hedberg and Klaus Mayer from ITU, Thomas Prohaska from BOKU-WIEN, Allan Pidduck and Michael Houlton from QinetiQ and Jane Poths from SAL for all constructive comments and feedback on this pilot NUSIMEP interlaboratory comparison campaign.

Abbreviations

AP	Additional Protocol
BOKU	Universität für Bodenkultur, University of Natural Resources and Applied Life Sciences
CITAC	Co-operation for International Traceability in Analytical Chemistry
CRM	Certified Reference Material
EC	European Commission
ES	Environmental Sampling
ESARDA	European Safeguards Research and Development Association
ESARDA WG DA	ESARDA Working Group on Standards and Techniques for Destructive Analysis
EU	European Union
EURACHEM	A focus for Analytical Chemistry in Europe
FT-TIMS	Fission Track Thermal Ionisation Mass Spectrometry
GC	Gas Chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
IAEA	International Atomic Energy Agency
ILC	Interlaboratory Comparison
IRMM	Institute for Reference Materials and Measurements
ISO	International Organisation for Standardisation
ITU	Institute for Transuranium Elements
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
LA-ICP-MS	Laser Ablation Multi Collector Inductively Coupled Plasma Mass Spectrometry
MS	Mass Spectrometry
NPT	Treaty on the Non-Proliferation of Nuclear Weapons
NUSIMEP	Nuclear Signatures Interlaboratory Measurement Evaluation Programme
NWAL	Network of Analytical Laboratories
REIMEP	Regular European Interlaboratory Measurement Evaluation Programme
SAL	Safeguards Analytical Laboratory
SEM	Scanning Electron Microscopy
SI	International System of Units
SIMS	Secondary Ion Mass Spectrometry

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Annexes

Annex 1: Invitation to nominate laboratories

EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

NUSIMEP

Geel, 30 January 2008
D04-IM(2008)D/2928

The IRMM Nuclear Signatures Interlaboratory Measurement Evaluation Programme

NUSIMEP-6: Uranium isotope amount ratios in uranium particles

NUSIMEP is an external quality control programme organised by IRMM with the object of providing materials for measurements of trace amounts of nuclear materials in environmental matrices.

Measurements of the isotopic ratios of the elements uranium and plutonium in small amounts, such as typically found in environmental samples, are required for nuclear safeguards, for the control of environmental contamination and for the detection of nuclear proliferation.

Several NUSIMEP comparison campaigns of measurements of uranium isotopic ratios were organised previously: for example NUSIMEP 2, uranium isotopic abundances in dry uranium nitrate samples; NUSIMEP 3, uranium isotopic abundances in saline media and NUSIMEP 4, uranium isotopic abundances in a simulated urine and NUSIMEP 5 uranium, plutonium and caesium isotopic ratios in saline medium.

We would like to announce the forthcoming NUSIMEP 6 interlaboratory comparison: "Uranium isotope amount ratios in uranium particles" and invite laboratories to participate.

Participating laboratories in NUSIMEP-6 receive a test sample of uranium particles on a graphite planchet with undisclosed isotope amount ratio values $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. The uranium isotope amount ratios are to be measured using their routine analytical procedures. Measurement of the major ratio $n(^{235}U)/n(^{238}U)$ is obligatory; measurements of the minor ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ are optional. The participants' measurement results will be evaluated against the certified reference values. Full confidentiality is guaranteed with respect to the link between measurement results and the participants' identity.

Participation fee is € 100, including dispatch. Due to the nature of this comparison only a limited number of samples are available. Samples will be allocated to participants in order of registration until the stock of NUSIMEP-6 samples is exhausted.

Please register electronically for this inter-laboratory comparison using the following link: http://www.irmm.jrc.be/imepapp/registerForComparison.action?comparison=94

Once you have submitted your registration electronically, please follow the procedure indicated: a) print your registration form; b) sign it; and c) fax it to us. Your fax is the confirmation of your participation.

The deadline for registration is **28 February 2008**. Samples will be sent to participants beginning of April 2008. The deadline for submission of results is 10 June 2008.

Please do not hesitate to contact us in case you need more information.

Yours sincerely,

Yetunde Aregbe

Jan Truyens
NUSIMEP-6 Co-ordinator

Yetunde Aregbe
IRMM Safeguards Co-ordinator

irmm
Institute for Reference Materials and Measurements

Retieseweg 111, 2440 Geel, Belgium
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jrc-irmm-im-nusimep@cec.eu.int • http://www.irmm.jrc.be

Annex 2: Confirmation of registration

From: TRUYENS Jan (JRC-GEEL)
Sent: donderdag 15 mei 2008 14:57
To: [redacted]
Subject: NUSIMEP-6: shipment of samples

Dear [redacted]

You were registered successfully for the Nuclear Signatures Interlaboratory Measurement Evaluation Programme: uranium isotope amount ratios in uranium particles. We are pleased to inform you that your NUSIMEP-6 sample has been dispatched. Within a couple of days it should arrive at your laboratory.

If you wish to track this shipment, you can check the process of delivery on the website of DHL (http://www.dhl.be) using the following tracking number: [redacted].

The sample consists of a graphite planchet covered with uranium particles with undisclosed isotope amount ratio values $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. The uranium isotope amount ratios are to be measured using your routine analytical procedures. Measurement of the major ratio $n(^{235}U)/n(^{238}U)$ is obligatory; measurements of the minor ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ are optional.
Your measurement results will be evaluated against the certified reference values. Full confidentiality is guaranteed with respect to the link between results and the participants' identity.

To login to the result reporting page you need a participant key and sample code, indicated on the accompanying letter to the sample. The sample code is also indicated on the sample box. Please read the accompanying letter carefully and store the participant key ([redacted]) and sample code ([redacted]) safely.

Please be aware of the **reporting deadline**, which is **10 July 2008**.

After we have received your "confirmation of receipt" form, we will send an invoice to pay the participation fee.

We wish you a lot of success with your measurements and please do not hesitate to contact us in case of any questions or problems.

Kind regards,

Jan Truyens
NUSIMEP-6 Co-ordinator

Yetunde Aregbe
IRMM Safeguards Co-ordinator

European Commission (EC) / Joint Research Centre (JRC)
Institute for Reference Materials and Measurements (IRMM)
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Retieseweg 111
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Belgium

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www.irmm.jrc.be

Annex 3: Instructions for measurement and reporting

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
Isotope measurements

NUSIMEP

Geel, 05 May 2008
Unit D04/IM/JTr D(08)10896

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS2»
«ADDRESS3»
«ZIP» «TOWN»
«COUNTRY»

NUSIMEP-6

Dear «TITLE» «SURNAME»,

Thank you very much for your participation in NUSIMEP-6.
Together with this letter we are sending to you the NUSIMEP-6 graphite planchet sample for particle analysis as specified in the NUSIMEP-6 announcement:

http://irmm.jrc.ec.europa.eu/html/interlaboratory_comparisons/nusimep/nusimep-6/index.htm

Please check whether the test material remained undamaged during transport. Then sign the "Confirmation of receipt" form and send it by email or fax it to us (Fax: +32 14 571 865).
The particles are separated by at least a few micrometers on average, although small agglomerates may also be present on the graphite planchet substrate. It is recommended to store the sample in a dry environment.

Your sample has a unique code: **«SAMPLECODE»**.

Participants in NUSIMEP are asked to apply the same measurement procedure as used in routine sample analysis of this kind.

You can find the reporting website at:

https://irmm.jrc.ec.europa.eu/ilc/ilcReporting.do

To access this webpage you need a personal password key, which is:

«PARTKEY»

The system will guide you through the reporting procedure. The result reporting page will be active from the end of May on. After entering your results, please also complete the questionnaire. Do not forget to submit and confirm always when required. Directly after submitting your results and after having filled out the questionnaire online, you will be prompted to print the completed report form. Please do so, sign the paper version and return it to IRMM by fax (at +32 14 571 865) or by e-mail. Check your results carefully for any errors before submission, since this is your definitive confirmation.

IRMM - Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32 (0)14 571 211. http://irmm.jrc.ec.europa.eu
Telephone: direct line +32 (0)14 571 976. Fax: +32 (0)14 571 865.

E-mail: jrc-irmm-im-nusimep@ec.europa.eu

./.

The deadline for submission of results is 10 July 2008.

Although we have no doubts about your professionalism, we would like to mention that collusion nullify the benefits of interlaboratory comparisons to customers, analysts and accreditation bodies.

Please do not hesitate to contact us in case you need more information.

Yours sincerely,

Jan Truyens
NUSIMEP-6 Co-ordinator

Yetunde Aregbe
IRMM Safeguards Co-ordinator

IRMM - Retieseweg 111, B-2440 Geel - Belgium. Telephone: +32 (0)14 571 211. http://irmm.jrc.ec.europa.eu
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E-mail: jrc-irmm-im-nusimep@ec.europa.eu

EUROPEAN COMMISSION
JOINT RESEARCH CENTRE

Institute for Reference Materials and Measurements
Isotope measurements

NUSIMEP

Geel, 05 May 2008
Annex to Unit D04/IM/JTr D(08)10896

«TITLE» «FIRSTNAME» «SURNAME»
«ORGANISATION»
«DEPARTMENT»
«ADDRESS»
«ADDRESS1»
«ADDRESS2»
«ADDRESS3»
«ZIP» «TOWN»
«COUNTRY»

NUSIMEP-6

Confirmation of receipt of the graphite planchet sample

Please return this form at your earliest convenience.

This confirms that the sample package arrived.

In case the package is damaged,

please state this on the form and contact us immediately.

ANY REMARKS ....
....

Date of package arrival ....

Signature ....

<u>Please return this form to:</u>
Jan Truyens
NUSIMEP-6 Co-ordinator
EC-JRC-IRMM
Retieseweg 111
B-2440 GEEL, Belgium
Fax : +32 14 571 865
e-mail : JRC-IRMM-IM-NUSIMEP@ec.europa.eu

Annex 4: Questionnaire

Comparison for NUSIMEP-6

PLEASE COMPLETE THIS FORM TOGETHER WITH THE RESULT REPORTING FORM. ALL ANSWERS WILL BE TREATED CONFIDENTIALLY (Non-disclosure of the identity of the laboratories)

Submission Form

1. **What is the mission of your laboratory? (more than one choice possible)** *

- a) Environmental sciences
- b) Measurements for fissile material control or safeguards
- c) Network of Analytical Laboratories (NWAL)
- d) Other

1.1. If you have selected 'Other', please specify:

2. **Is your laboratory certified, accredited or authorised for this type of analysis? (more than one c**

- a) Accredited
- b) Authorised
- c) Certified

3. **Is your laboratory working according to a quality management system?** *

- a) Yes
- b) No

3.1. If 'Yes' please specify:

- a) ISO 17025
- b) ISO 9000 series
- c) Other

3.1.1. If 'Other' please specify:

4. **Does your laboratory participate in inter-laboratory comparisons?** *

- a) Yes
- b) No

4.1. If 'Yes', please list the name(s) of the comparison(s) and organizer(s):

5. **How many measurement of this type does your laboratory routinely perform per year?** *

- a) 0-10
- b) 11-50
- c) 51-100
- d) >100

6. **How does your laboratory rate itself for these types of measurement?** *

- a) Experienced
- b) Less experienced
- c) Not experienced

7. **Was the NUSIMEP-6 sample treated according to the same analytical procedure routinely used for this** *

- a) Yes
- b) No

7.1. If 'No' please specify why not:

8. **Was a chemical treatment applied to the NUSIMEP-6 sample?** *

- a) Yes
- b) No

8.1. If 'Yes' please specify

9. **How did you select (scan) the particle(s) for your measurements?** *

- a) FT
- b) SEM-EDX
- c) SIMS

9.1. Please give a brief description on the particle selection: *

10. **Was a particle transfer needed?** *

- a) Yes
- b) No

10.1. If 'Yes' please describe the particle transfer:

11. **Does your laboratory routinely use Certified Reference Materials?** *

- a) Yes
- b) No

11.1. If 'Yes' please specify which CRMs and suppliers:

11.2. How are the CRMs applied? *

- a) Calibration of instrument
- b) Validation of procedure
- c) Other

11.2.1. If 'Other' please specify:

12. **Did you apply a correction for mass fractionation / mass bias to your measurement results?** *

- a) Yes
- b) No

12.1. If "Yes", how was the mass fractionation determined?

13. **Did you use Secondary Ion Mass Spectrometry (SIMS) to analyse the uranium particles?** *

- a) Yes
- b) No

13.1. If 'Yes', please provide the following information on the instrument parameters:

13.2. Type of SIMS used (brand, model,..):

13.3. Primary ion beam and primary ion beam accelerating energy:

13.4. Secondary ion extraction kV:

13.5. Mass resolution used:

13.6. Secondary ion energy window:

13.7. EM detector type:

13.8. Dead time correction applied?

- [ ] a) Yes
- [ ] b) No

13.8.1. If 'Yes' report the dead time:

14. **Did you use Secondary Ion Mass Spectrometry (SIMS) to analyse the uranium particles?** *

- [ ] a) Yes
- [ ] b) No

14.1. If 'Yes', please provide the following information on the measurement conditions:

14.2. Presputter conditions (before microprobe measurements)

14.3. Microprobe measurement conditions:

14.4. Spot size (estimated diameter):

14.5. Raster size (if used):

14.6. Masses cycled & cycle times:

14.7. Total sputter time per measurement:

15. **Did you use Secondary Ion Mass Spectrometry (SIMS) to analyse the uranium particles?** *

- [ ] a) Yes
- [ ] b) No

15.1. If 'Yes', please provide the following information for each measurement:

15.2. 238U signal level from particle at start (cps):

15.3. 238U signal level from particle at end (cps)

15.4. Comment on stability of signal levels during microprobe: stable, decreasing, increasing, variable?

15.5. Comments on appearance of U ion image field (if possible): clear particles?, diffuse spots?, unifor

16. **Did you use Thermal Ionisation Mass Spectrometry (TIMS) to analyse the uranium particles?** *

- [ ] a) Yes
- [ ] b) No

16.1. If 'Yes', please provide the following information on the instrument parameters:

16.2. Type of TIMS used (brand, model,..):

16.3. Detector used (brand):

16.4. Please provide information on detector used:

- a) Analogue detector operation mode
- b) Channeltron (contiuous dynode SEM)
- c) Discrete dynode SEM
- d) Ion counting detector operation mode
- e) multiple detectors used
- f) Single detector used

16.5. Dead time correction applied?

- a) Yes
- b) No

16.5.1. If 'Yes' report the dead time:

16.6. Did you apply any other correction to the detector output (e.g. SEM non-linearity correction)?

- a) Yes
- b) No

16.6.1. If 'Yes' please specify:

16.7. Specify filament type used:

- a) Single filament technique
- b) Double filament technique
- c) Zone refined Re
- d) Not zone refined Re
- e) Tungsten
- f) Other

16.7.1. If 'other' please specify:

17. **Did you use Thermal Ionisation Mass Spectrometry (TIMS) to analyse the uranium particles?** *

- a) Yes
- b) No

17.1. If 'Yes', please provide the following information for each measurement:

17.2. Measurement of single/multiple particles?

- a) Single particles
- b) Multiple particles

17.3. 238U average signal level

17.4. Overall ionisation efficiency (estimate)

18. **Did you use Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to analyse the** *

- a) Yes
- b) No

18.1. If 'Yes', please provide the following information on the instrument parameters:

18.2. Type of carrier gas used? (He (%), Ar (%), other)

18.3. Combination with nebulizer?

- a) Yes
- b) No

18.3.1. If 'Yes' please specify type of nebulizer:

18.4. LA carrier introduced into nebulizer or additional mixing of nebulizer?

18.5. Gas flow after LA cell:

18.6. Type of laser:

18.7. Laser wavelength (nm):

18.8. Energy flux (J/cm2):

18.9. Spot size (micrometer):

18.10. Repetition rate (Hz):

18.11. Ablation type (single spot, line scan, other...):

18.12. Type of instrument:

- a) ICP-HR-MS (single collector, high resolution)
- b) ICP-Q-MS (single collector, quadrupole)
- c) ICP-SF-MS (single coll., sector field, using low resolution (<1000))
- d) MC-ICP-MS (multi collector)

18.13. Type of detector used for each isotope (SEM, channeltron, Faraday cup):

19. **Are your reported uncertainties in NUSIMEP-6 calculated according to the Guides for Quantifying Mea** *

- a) Yes
- b) No

19.1. If 'No', how was the measurement uncertainty evaluated?

20. **Do you routinely report uncertainties on chemical measurements to your customers?** *

- a) Yes
- b) No

21. **Would you be interested in participating in future NUSIMEP Inter-laboratory comparisons on particle** *

- a) Yes
- b) No

21.1. If 'Yes', in what type of samples would you be interested (U, Pu, U/Pu)?

21.2. If 'Yes', what should be the particle density on the sample?

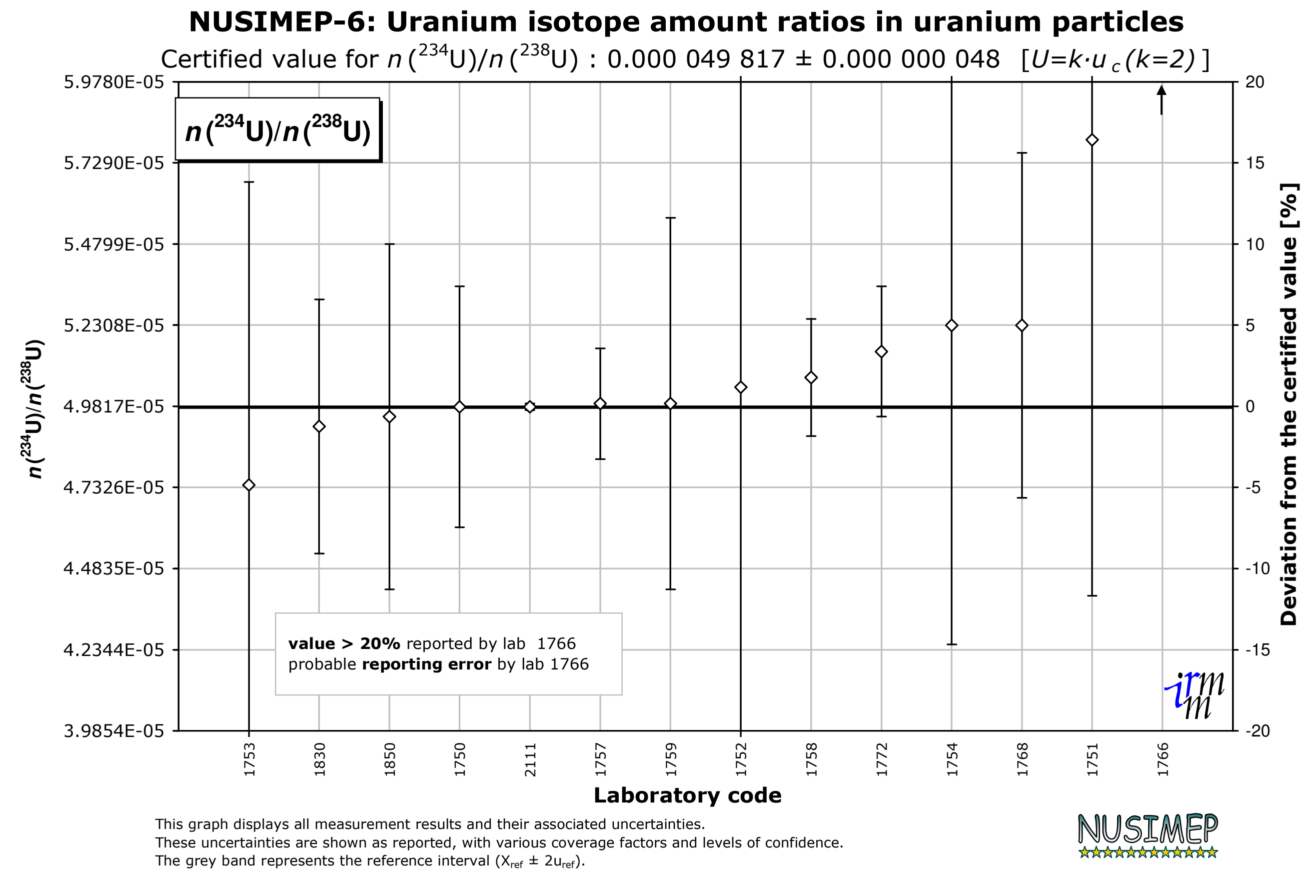
21.3. If 'Yes', Which isotopic composition (enrichment)?

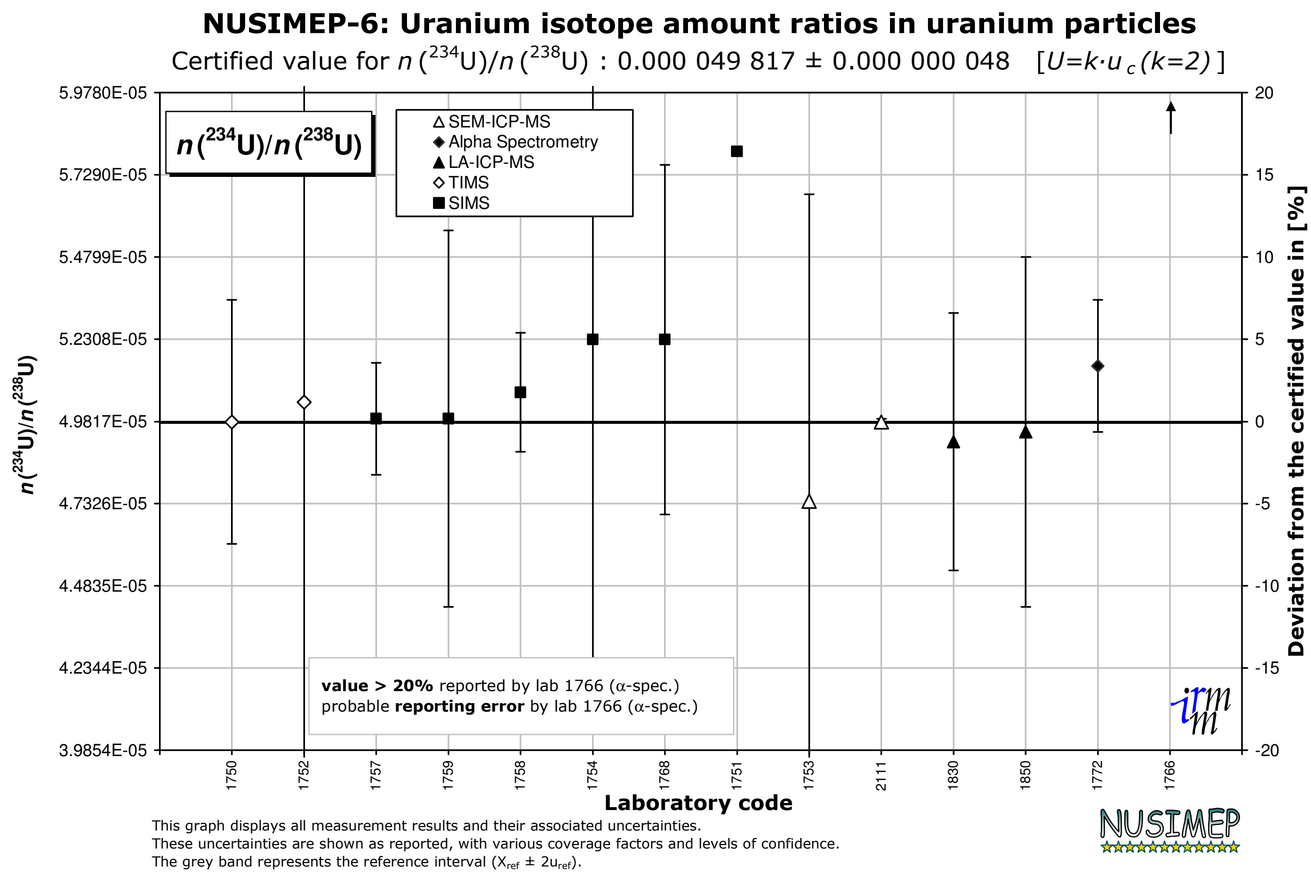
21.4. If 'Yes', would it be of interest to you to analyse uranium oxyfluoride particles?

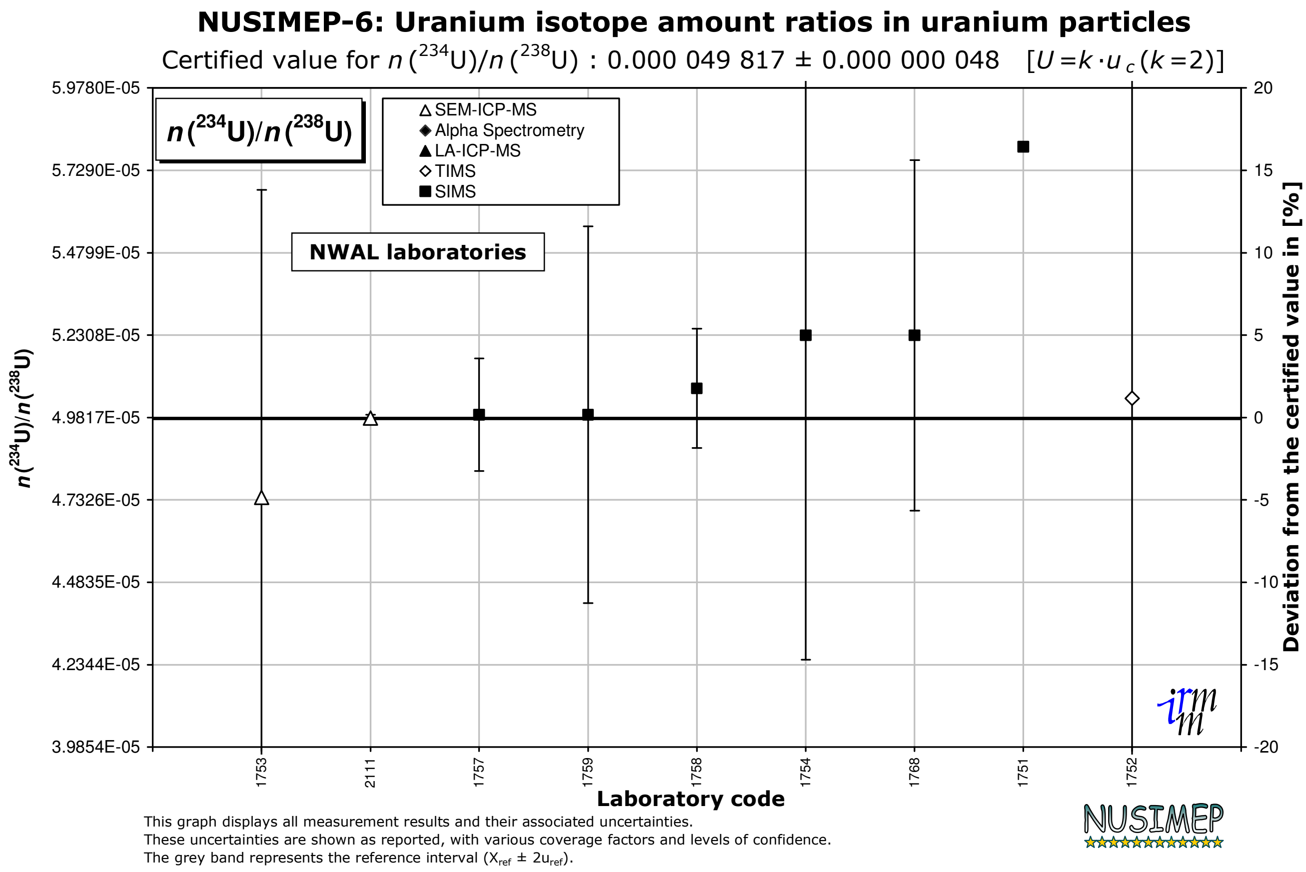
22. **Do you have any other feedback/comments on NUSIMEP-6?**

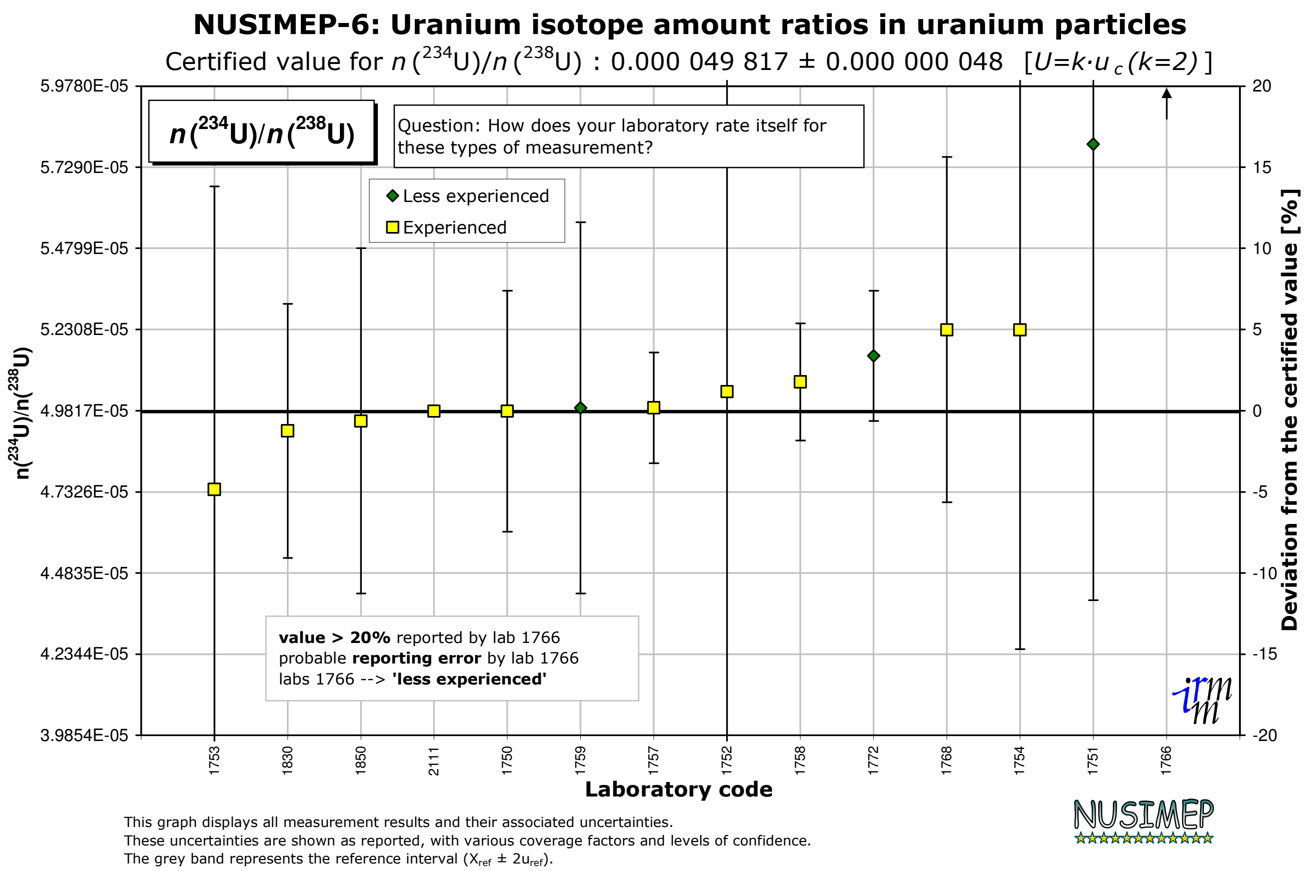
Annex 5: Results for $n(^{234}U)/n(^{238}U)$

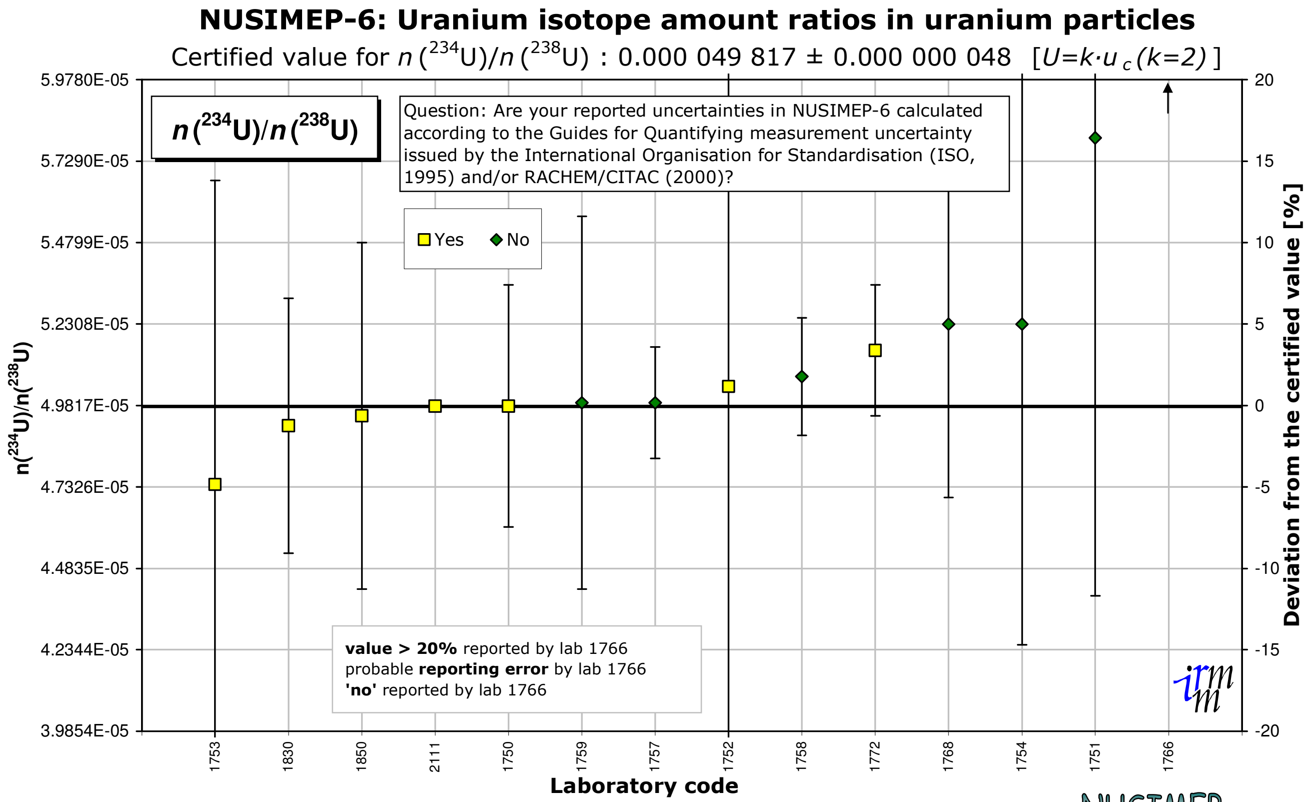
Laboratory	Analytical method	Reported $n(^{234}U)/n(^{238}U)$	Reported uncertainty $n(^{234}U)/n(^{238}U)$	Coverage factor k	z score	zeta score
1749	SIMS Microprobe					
1750	TIMS	0.0000498	0.0000037	2	-0.01	-0.01
1751	SIMS	0.000058	0.000014	17	3.29	9.93
1752	TIMS	0.0000504	0.0000194	2	0.23	0.06
1753	ICP-MS	0.0000474	0.0000093	2	-0.97	-0.52
1754	SIMS	0.0000523	0.0000098	2	1.00	0.51
1755	SIMS					
1756	FT-TIMS					
1757	SIMS	0.0000499	0.0000017	1	0.03	0.05
1758	SIMS	0.0000507	0.0000018	2	0.35	0.98
1759	SIMS	0.0000499	0.0000057	2	0.03	0.03
1766	Alpha Spectrometry	0.825	0.0001	2	331192.24	16499.00
1767	SIMS					
1768	SIMS	0.0000523	0.0000053	2.13	1.00	1.00
1770	LA-ICP-SF-MS					
1772	Alpha Spectrometry	0.0000515	0.000002	1	0.68	0.84
1830	LA-MC-ICP-MS	0.0000492	0.0000039	2	-0.25	-0.32
1850	LA-MC-ICP-MS	0.0000495	0.0000053	1	-0.13	-0.06
2110	NanoSIMS					
2111	MC-ICP-MS	0.0000498	0.0000001	2	-0.01	-0.31


NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for $n(^{234}U)/n(^{238}U)$: 0.000 049 817 ± 0.000 000 048 [$U=k \cdot u_c(k=2)$]
$n(^{234}U)/n(^{238}U)$
value > 20% reported by lab 1766
probable reporting error by lab 1766
Laboratory code
Deviation from the certified value [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).


NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for $n(^{234}U)/n(^{238}U)$: 0.000 049 817 ± 0.000 000 048 [$U=k \cdot u_c(k=2)$]
$n(^{234}U)/n(^{238}U)$
SEM-ICP-MS
Alpha Spectrometry
LA-ICP-MS
TIMS
SIMS
value > 20% reported by lab 1766 (α-spec.)
probable reporting error by lab 1766 (α-spec.)
Laboratory code
Deviation from the certified value in [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).


NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n(234U)/n(238U) : 0.000 049 817 ± 0.000 000 048 [U=k·uc(k=2)]
n(234U)/n(238U)
SEM-ICP-MS
Alpha Spectrometry
LA-ICP-MS
TIMS
SIMS
NWAL laboratories
Laboratory code
Deviation from the certified value in [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).
NUSIMEP

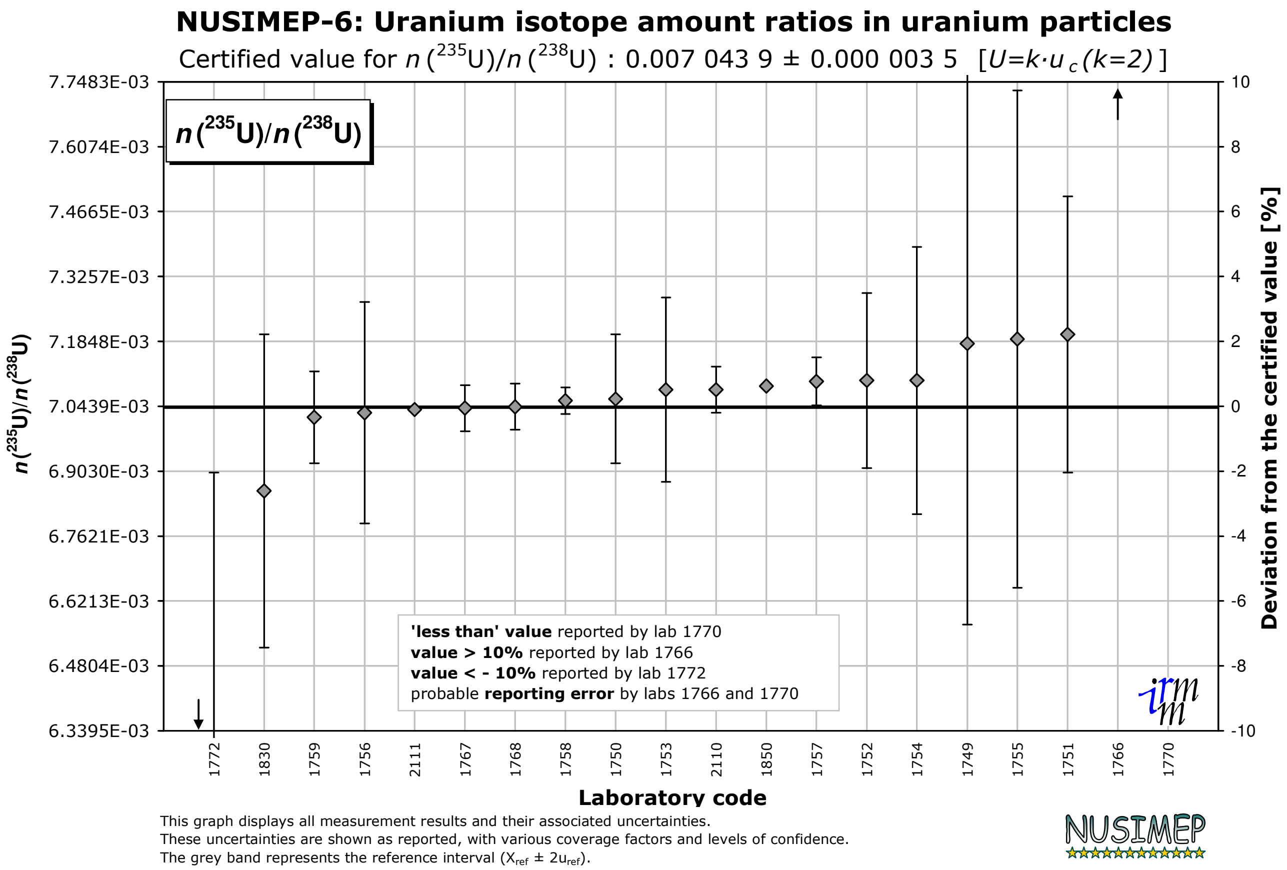

NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n(234U)/n(238U) : 0.000 049 817 ± 0.000 000 048 [U=k·uc(k=2)]
n(234U)/n(238U)
Question: How does your laboratory rate itself for these types of measurement?
Less experienced
Experienced
value > 20% reported by lab 1766
probable reporting error by lab 1766
labs 1766 --> 'less experienced'
Laboratory code
Deviation from the certified value [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).
NUSIMEP

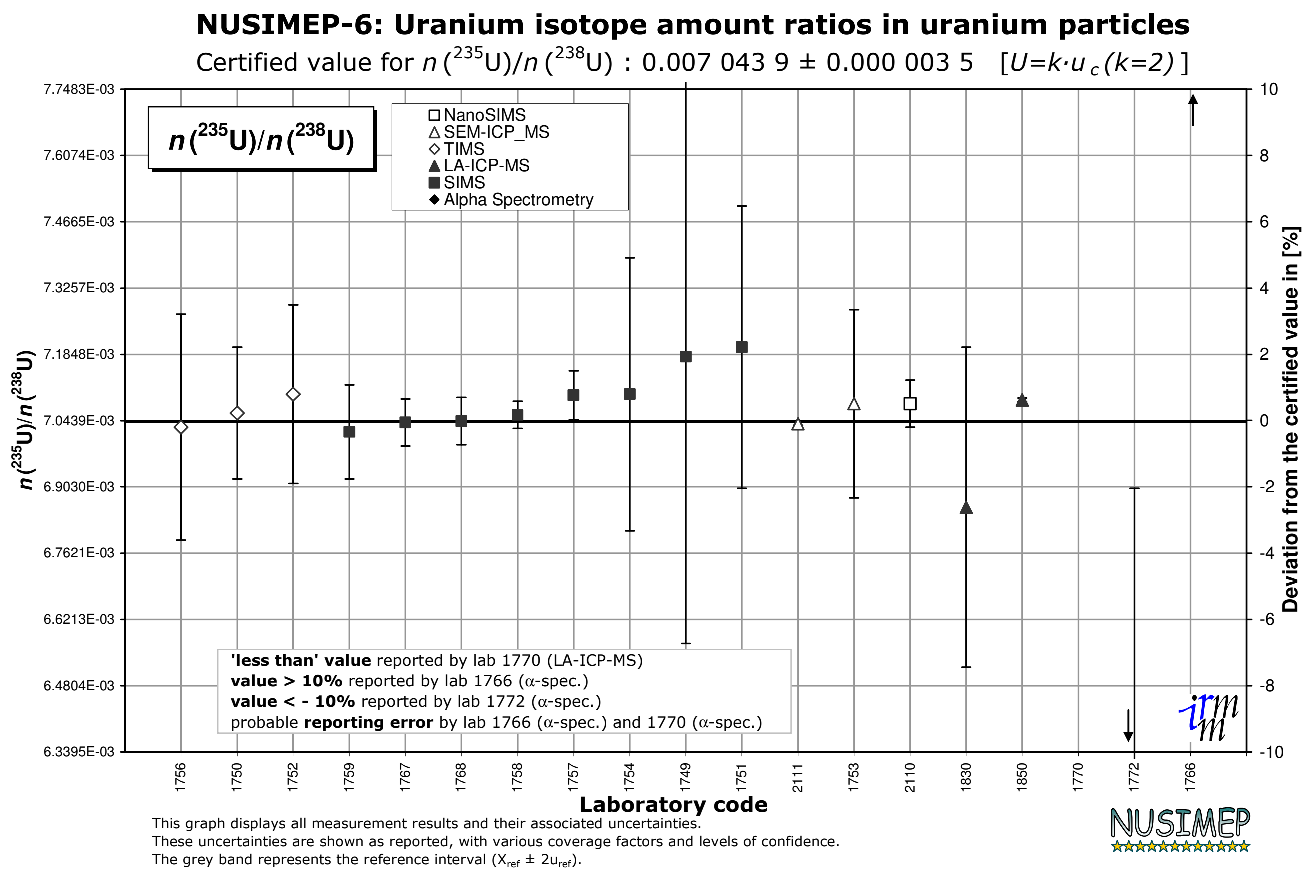


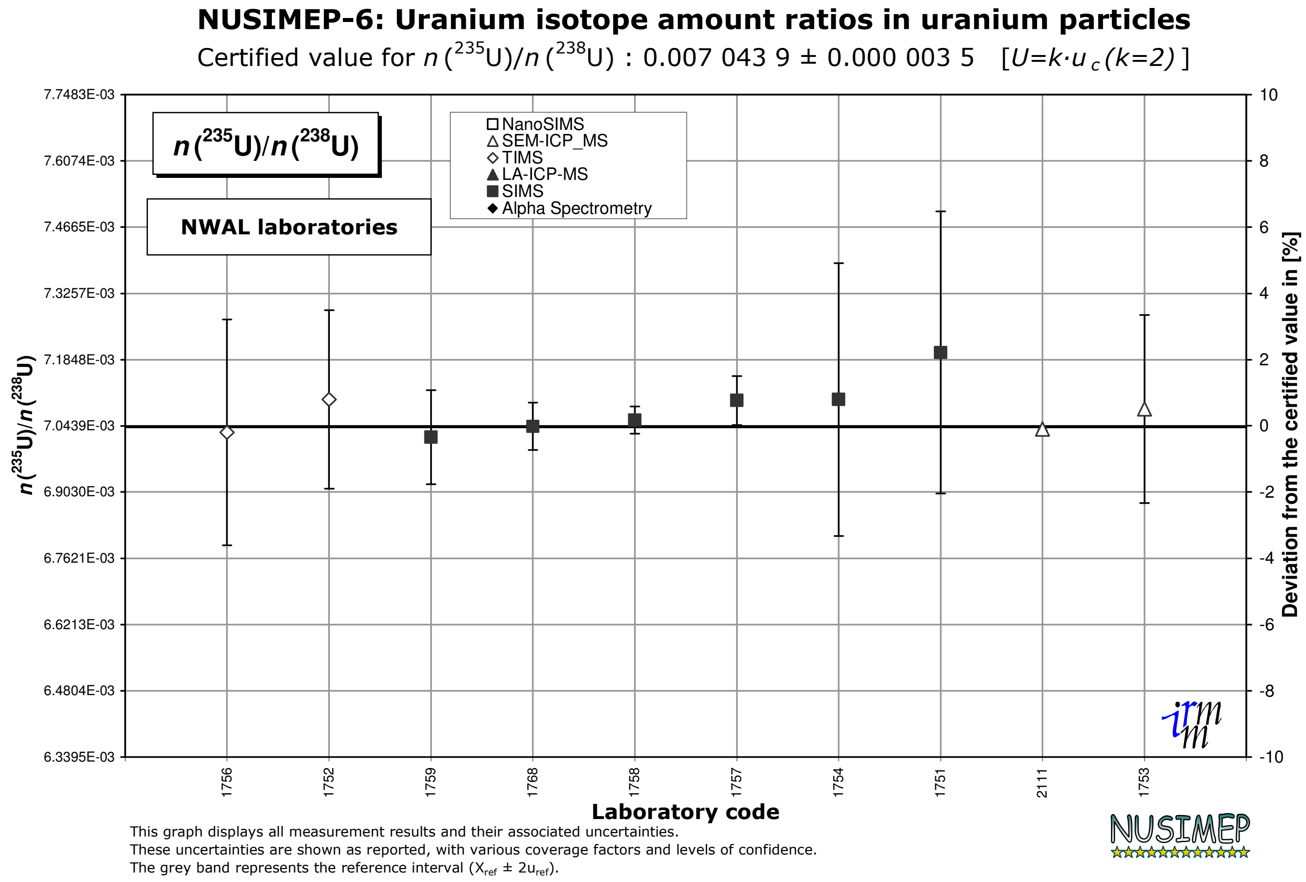
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).

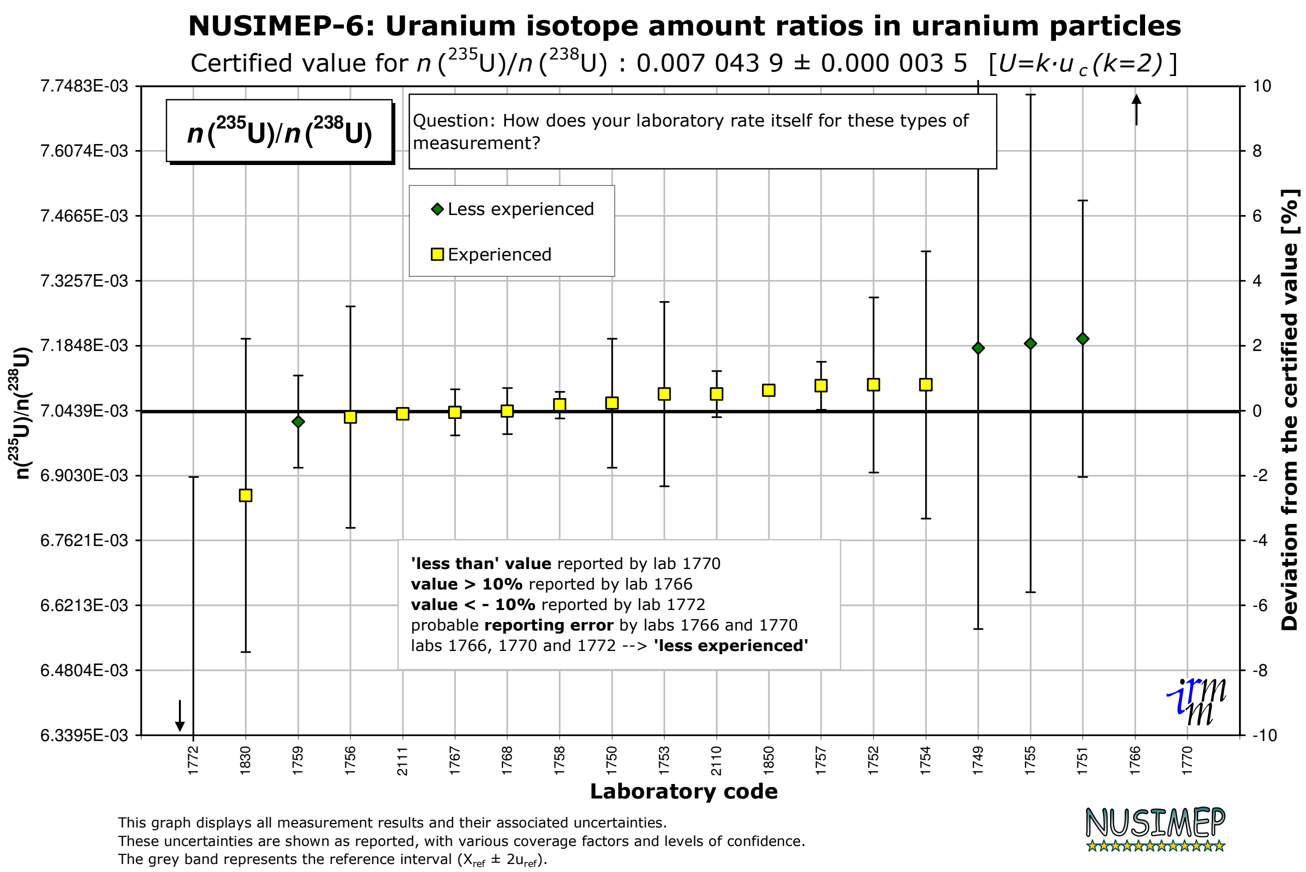
Annex 6: Results for $n(^{235}U)/n(^{238}U)$

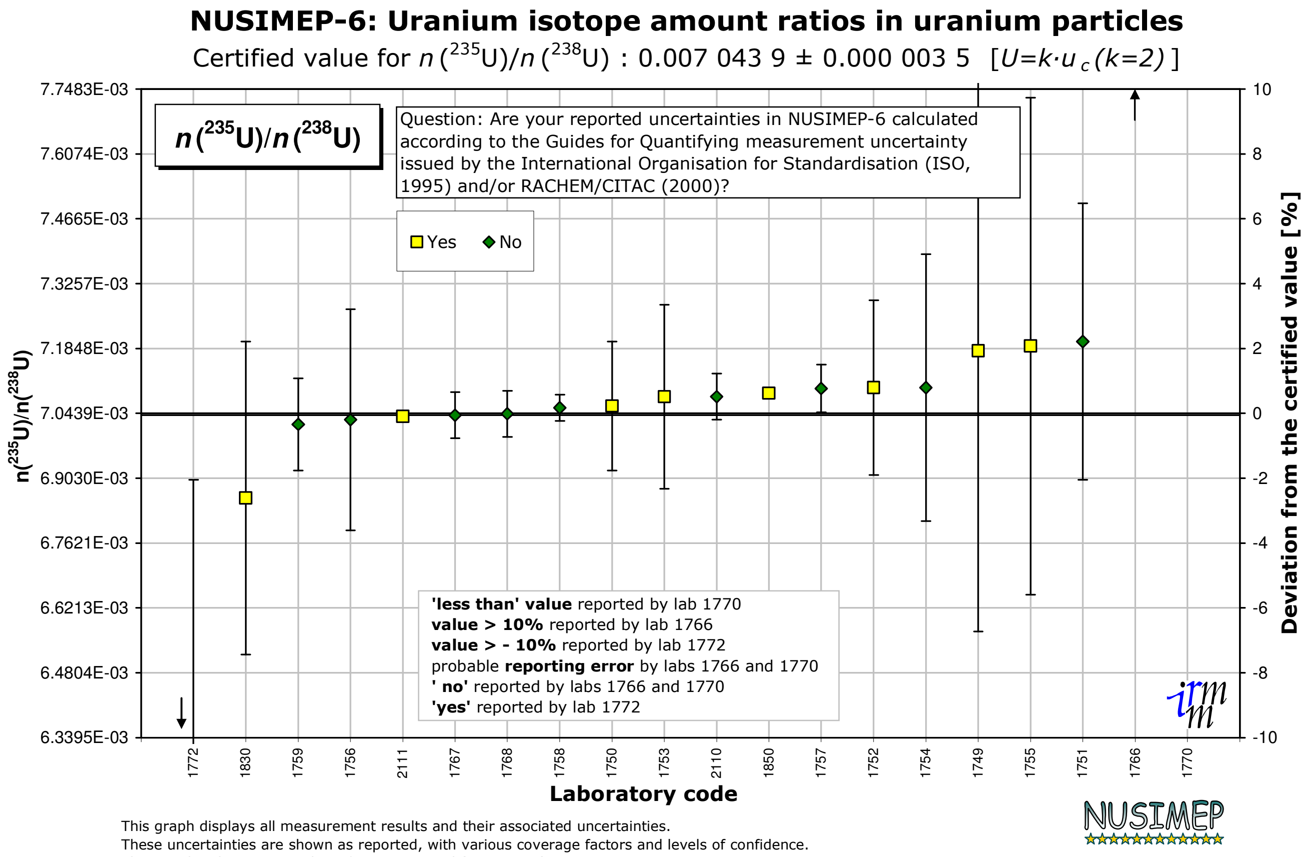
Laboratory	Analytical method	Reported $n(^{235}U)/n(^{238}U)$	Reported uncertainty $n(^{235}U)/n(^{238}U)$	Coverage factor k	z score	zeta score
1749	SIMS Microprobe	0.00718	0.00061	2	1.93	0.45
1750	TIMS	0.00706	0.00014	2	0.23	0.23
1751	SIMS	0.0072	0.0003	61	2.22	29.90
1752	TIMS	0.0071	0.00019	2	0.80	0.59
1753	ICP-MS	0.00708	0.0002	2	0.51	0.36
1754	SIMS	0.0071	0.00029	2	0.80	0.39
1755	SIMS	0.00719	0.00054	2	2.07	0.54
1756	FT-TIMS	0.00703	0.00024	1	-0.20	-0.06
1757	SIMS	0.007098	0.000052	1	0.77	1.04
1758	SIMS	0.007056	0.0000288	2	0.17	0.83
1759	SIMS	0.00702	0.0001	2	-0.34	-0.48
1766	Alpha Spectrometry	0.066	0.004	2	836.98	29.48
1767	SIMS	0.00704	0.00005	2	-0.06	-0.16
1768	SIMS	0.007043	0.00005	2.13	-0.01	-0.04
1770	LA-ICP-SF-MS	<108	0			
1772	Alpha Spectrometry	0.0058	0.0011	1	-17.66	-1.13
1830	LA-MC-ICP-MS	0.00686	0.00034	2	-2.61	-1.08
1850	LA-MC-ICP-MS	0.007088	0.0000045	1	0.62	9.09
2110	NanoSIMS	0.00708	0.00005	2	0.51	1.44
2111	MC-ICP-MS	0.007037	0.000003	2	-0.10	-2.99


NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n (235U)/n (238U) : 0.007 043 9 ± 0.000 003 5 [U=k·u c (k=2)]
n (235U)/n (238U)
'less than' value reported by lab 1770
value > 10% reported by lab 1766
value < - 10% reported by lab 1772
probable reporting error by labs 1766 and 1770
Laboratory code
Deviation from the certified value [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).
NUSIMEP


NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n (235U)/n (238U) : 0.007 043 9 ± 0.000 003 5 [U=k·u c (k=2)]
n (235U)/n (238U)
NanoSIMS
SEM-ICP_MS
TIMS
LA-ICP-MS
SIMS
Alpha Spectrometry
'less than' value reported by lab 1770 (LA-ICP-MS)
value > 10% reported by lab 1766 (α-spec.)
value < - 10% reported by lab 1772 (α-spec.)
probable reporting error by lab 1766 (α-spec.) and 1770 (α-spec.)
Laboratory code
Deviation from the certified value in [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).
NUSIMEP


NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n(235U)/n(238U) : 0.007 043 9 ± 0.000 003 5 [U=k·uc(k=2)]
n(235U)/n(238U)
NWAL laboratories
NanoSIMS
SEM-ICP_MS
TIMS
LA-ICP-MS
SIMS
Alpha Spectrometry
Laboratory code
Deviation from the certified value in [%]
NUSIMEP
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).

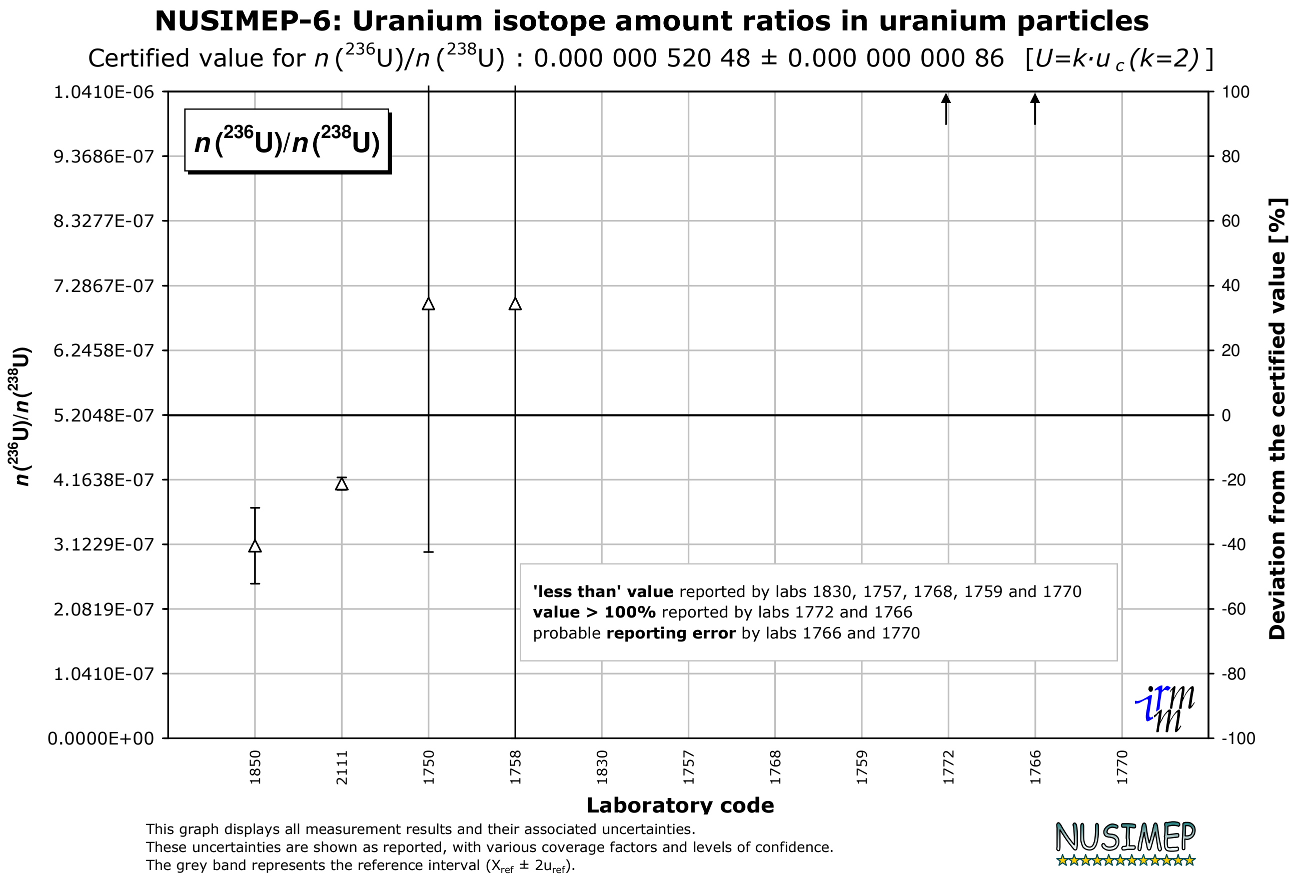

NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n(235U)/n(238U) : 0.007 043 9 ± 0.000 003 5 [U=k·uc(k=2)]
n(235U)/n(238U)
Question: How does your laboratory rate itself for these types of measurement?
Less experienced
Experienced
'less than' value reported by lab 1770
value > 10% reported by lab 1766
value < - 10% reported by lab 1772
probable reporting error by labs 1766 and 1770
labs 1766, 1770 and 1772 --> 'less experienced'
Laboratory code
Deviation from the certified value [%]
NUSIMEP
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).

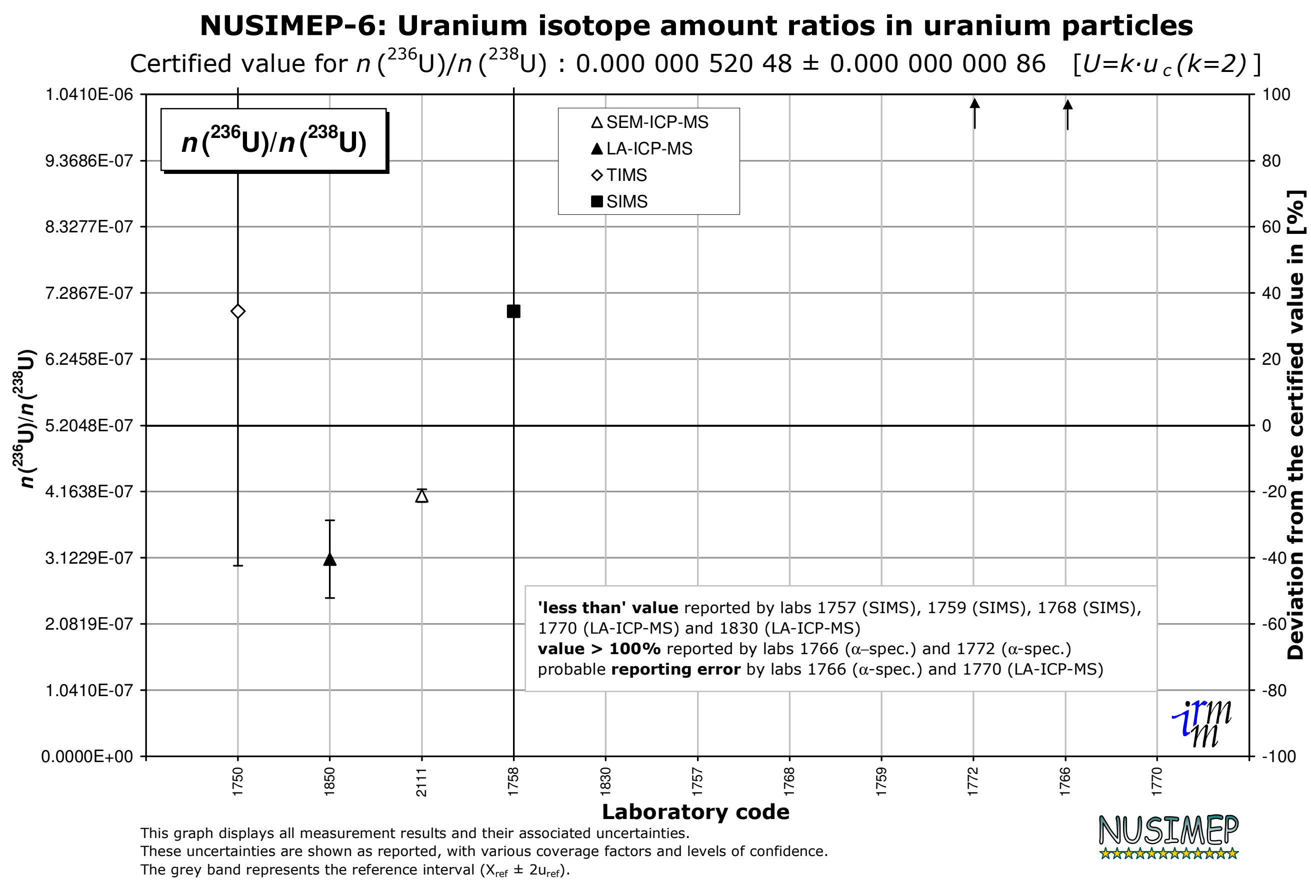


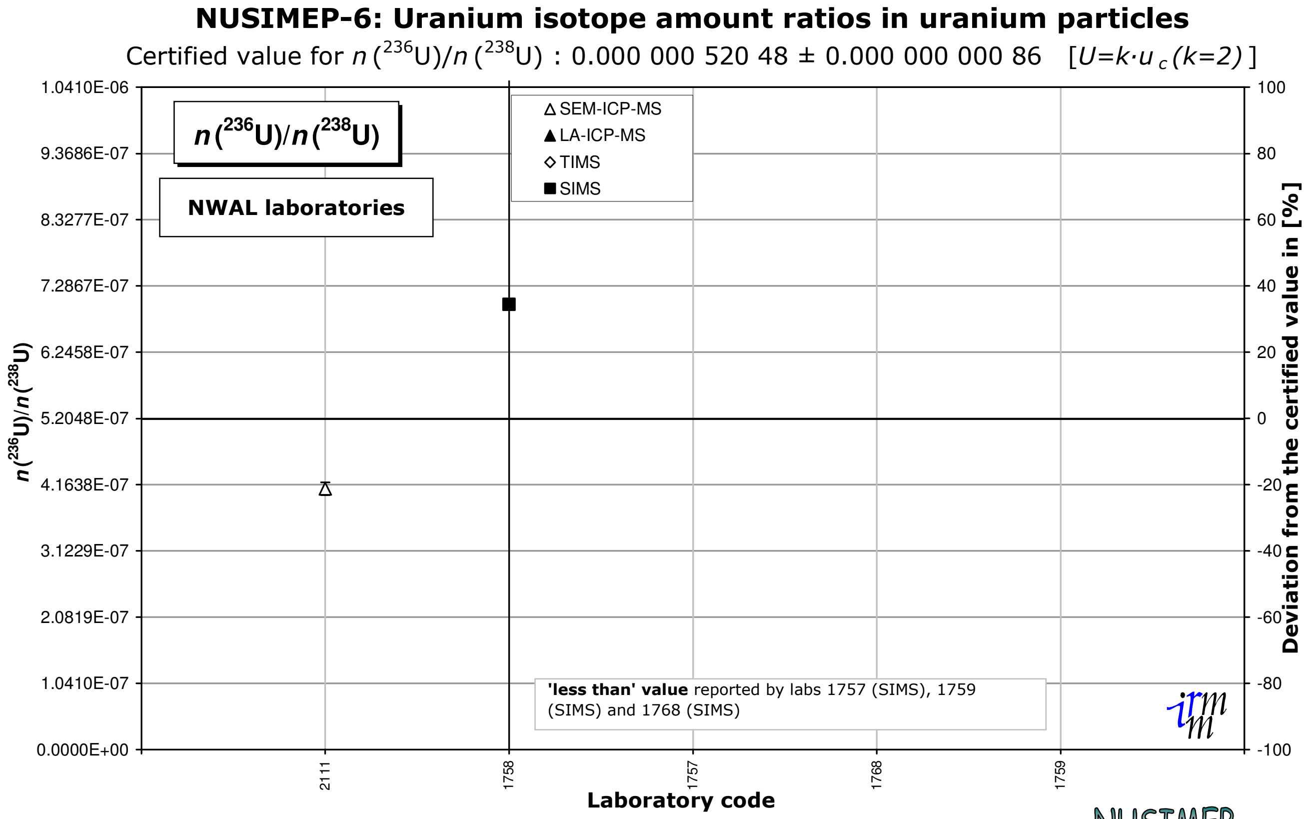
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).

Annex 7: Results for $n(^{236}U)/n(^{238}U)$

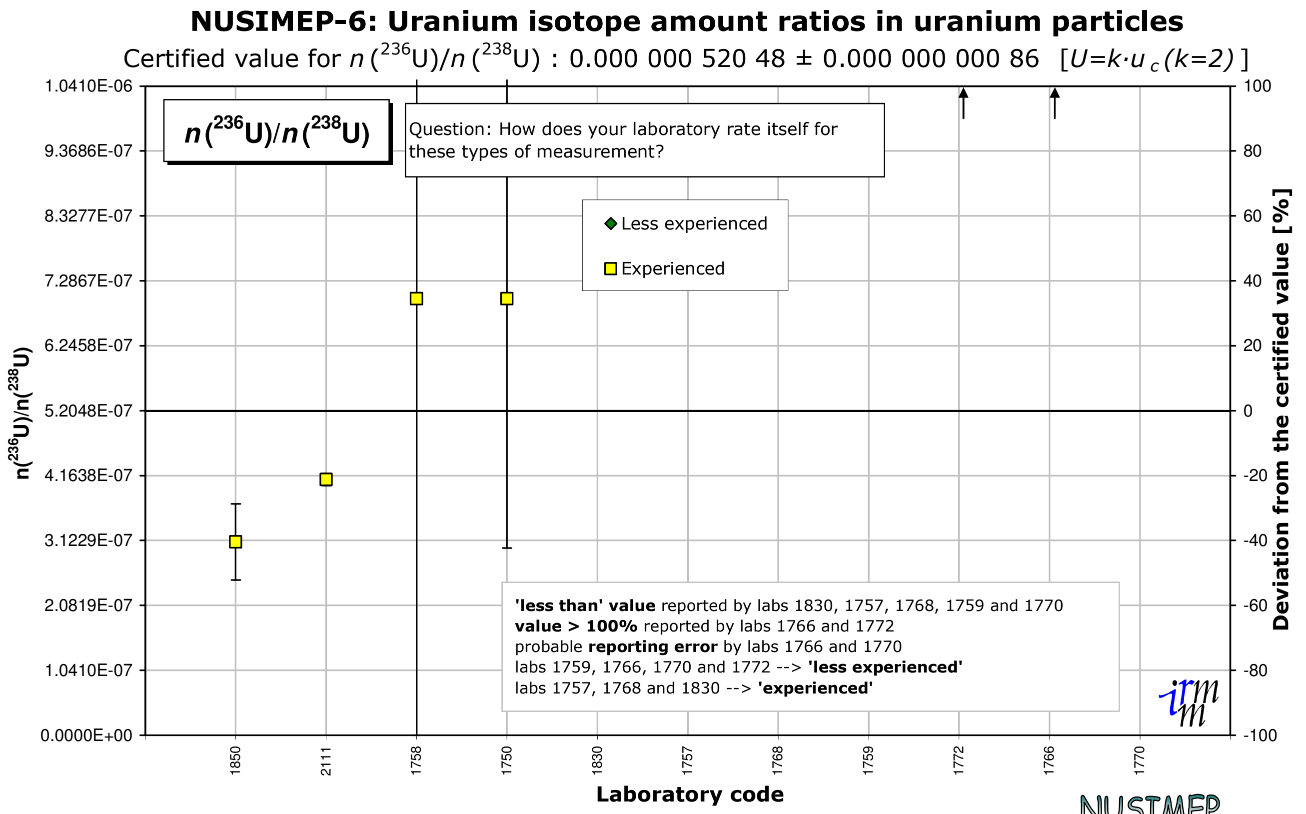
Laboratory	Analytical method	Reported $n(^{236}U)/n(^{238}U)$	Reported uncertainty $n(^{236}U)/n(^{238}U)$	Coverage factor *k*	z score	zeta score
1749	SIMS Microprobe					
1750	TIMS	0.0000007	0.0000004	2	1.38	0.90
1751	SIMS					
1752	TIMS					
1753	ICP-MS					
1754	SIMS	< 0				
1755	SIMS					
1756	FT-TIMS					
1757	SIMS	< 0.0000037				
1758	SIMS	0.0000007	0.0000007	2	1.38	0.51
1759	SIMS	< 0.000025				
1766	Alpha Spectrometry	0.017	0.008	2	130644.63	4.25
1767	SIMS					
1768	SIMS	< 0.0000083				
1770	LA-ICP-SF-MS	< 800				
1772	Alpha Spectrometry	0.00007	0.00005	1	533.96	1.39
1830	LA-MC-ICP-MS	< 0.000003				
1850	LA-MC-ICP-MS	0.00000031	0.000000061	1	-1.62	-3.45
2110	NanoSIMS					
2111	MC-ICP-MS	0.00000041	0.00000001	2	-0.85	-


NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n(236U)/n(238U) : 0.000 000 520 48 ± 0.000 000 000 86 [U=k·uc(k=2)]
n(236U)/n(238U)
'less than' value reported by labs 1830, 1757, 1768, 1759 and 1770
value > 100% reported by labs 1772 and 1766
probable reporting error by labs 1766 and 1770
Laboratory code
Deviation from the certified value [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).
NUSIMEP

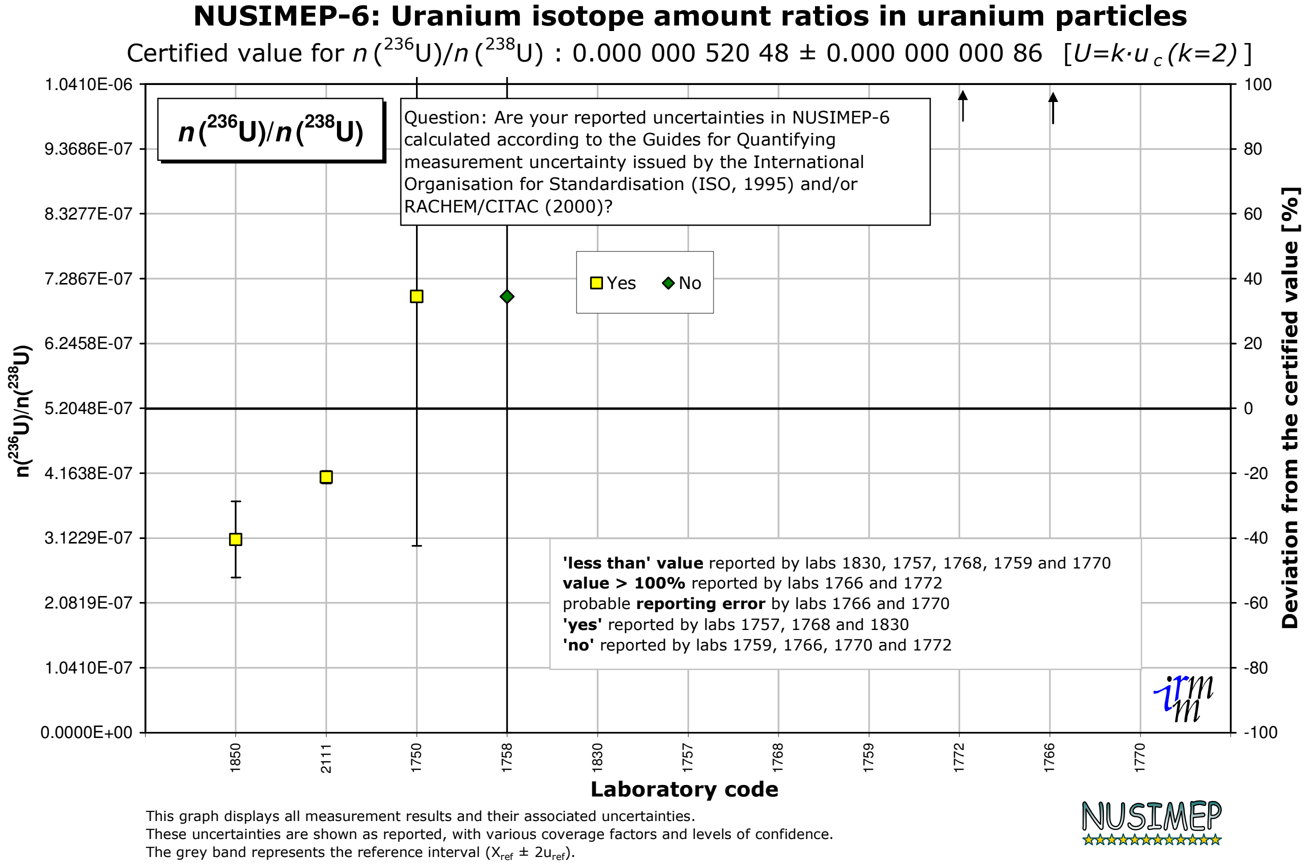

NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n(236U)/n(238U) : 0.000 000 520 48 ± 0.000 000 000 86 [U=k·uc(k=2)]
n(236U)/n(238U)
SEM-ICP-MS
LA-ICP-MS
TIMS
SIMS
'less than' value reported by labs 1757 (SIMS), 1759 (SIMS), 1768 (SIMS), 1770 (LA-ICP-MS) and 1830 (LA-ICP-MS)
value > 100% reported by labs 1766 (α–spec.) and 1772 (α-spec.)
probable reporting error by labs 1766 (α-spec.) and 1770 (LA-ICP-MS)
Laboratory code
Deviation from the certified value in [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).
NUSIMEP



This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).



This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval ($X_{ref} \pm 2u_{ref}$).


NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Certified value for n(236U)/n(238U) : 0.000 000 520 48 ± 0.000 000 000 86 [U=k·uc(k=2)]
n(236U)/n(238U)
Question: Are your reported uncertainties in NUSIMEP-6 calculated according to the Guides for Quantifying measurement uncertainty issued by the International Organisation for Standardisation (ISO, 1995) and/or RACHEM/CITAC (2000)?
Yes
No
'less than' value reported by labs 1830, 1757, 1768, 1759 and 1770
value > 100% reported by labs 1766 and 1772
probable reporting error by labs 1766 and 1770
'yes' reported by labs 1757, 1768 and 1830
'no' reported by labs 1759, 1766, 1770 and 1772
1.0410E-06
9.3686E-07
8.3277E-07
7.2867E-07
6.2458E-07
5.2048E-07
4.1638E-07
3.1229E-07
2.0819E-07
1.0410E-07
0.0000E+00
100
80
60
40
20
0
-20
-40
-60
-80
-100
1850
2111
1750
1758
1830
1757
1768
1759
1772
1766
1770
Laboratory code
Deviation from the certified value [%]
This graph displays all measurement results and their associated uncertainties.
These uncertainties are shown as reported, with various coverage factors and levels of confidence.
The grey band represents the reference interval (Xref ± 2uref).
NUSIMEP

Annex 8: Certificate

EUROPEAN COMMISSION
DIRECTORATE GENERAL JRC
JOINT RESEARCH CENTRE
IRMM
Institute for Reference Materials and Measurements

CERTIFICATE of a reference measurement

IM/MeaC/06/04-IMN-10123
2 December 2004

1. Applicant: R Wellum, IRMM

2. Sample Identification:
   - LOT 2435
   - Chemical form: UF_6, and Uranium Nitrate
   - IM sample registration number: IMN-10123

3. Measurands:
   - Isotopic composition

isotope amount ratio(s)	
$n(^{234}U)/n(^{238}U)$	0.000 049 817(48)
$n(^{235}U)/n(^{238}U)$	0.007 043 9(35)
$n(^{236}U)/n(^{238}U)$	0.000 000 520 48(86)

amount fraction (·100)		mass fraction (·100)	
$n(^{234}U)/n(U)$	0.004 946 6(47)	$m(^{234}U)/m(U)$	0.004 863 7(46)
$n(^{235}U)/n(U)$	0.699 43(35)	$m(^{235}U)/m(U)$	0.690 66(34)
$n(^{236}U)/n(U)$	0.000 051 682(85)	$m(^{236}U)/m(U)$	0.000 051 251(84)
$n(^{238}U)/n(U)$	99.295 57(35)	$m(^{238}U)/m(U)$	99.304 43(35)

molar mass: 238.029553(11) $g \cdot mol^{-1}$

4. Date of receipt of sample : 1 April 2004
   Date of completion of measurement : 26 May 2004

5. Uncertainty:
All uncertainties indicated are expanded uncertainties $U = k \cdot u_c$ where u_c is the combined standard uncertainty calculated according to the ISO/BIPM guide. They are given in parentheses and include a coverage factor k=2. They apply to the last two digits of the value. The values certified are traceable to the SI.
The primary certified values are the isotope amount ratios; other values are derived from them. Reproducing the derived values may result in differences due to rounding errors.

6. The traceability to SI is established through UF_6-standards as IRMM 071 and IRMM 711.

7. Analytical measurement procedure

- Mass spectrometric measurements were performed by W De Bolle for the $[n(^{235}U)/n(^{238}U)]$ isotope ratio using the MAT511 mass spectrometer on UF_6 samples prepared by A Moens and W De Bolle. TIMS measurements on $[n(^{234}U)/n(^{238}U)]$ and $[n(^{236}U)/n(^{238}U)]$ were performed by S Richter, H Kuehn and A Alonso using the TRITON on samples chemically prepared by A Alonso. A Verbruggen was responsible for the preparation and issuance of the certificate.
- The atomic masses, used in the calculations, are from G. Audi and A.H. Wapstra, The 1993 atomic mass evaluation , Nucl Phys A565 (1993) 1-65.
- Reference number of the measurement data: measurement number T4504, logged in S:\Im UNIT\Secure Data\Archive MS Measurements data files\TRITON\data.

Stephan Richter
Task leader

Copies:
P Taylor, IM Unit Head
R Wellum
A Alonso
H Kühn
A Moens
Archive

Retieseweg, B-2440 Geel, BelgiumTel.: +32-(0)14-571 211 • Fax: +32-(0)14-584 273 • http://www.irmm.jrc.be

Annex 9: Summary of the information given by the participants on instrument parameters and measurement conditions for SIMS, TIMS and LA-ICP-MS

SIMS: parameters	
Type of SIMS used (brand, model,..)	
	CAMECA IMS3f
	Cameca IMS-4f
	CAMECA IMS-6F
	CAMECA IMS 6f
	Cameca IMS 7f
	4FE6
	CAMECA 4f with PSEARCH
	CAMECA 3f (upgraded to 4f capabilities).
	Cameca IMS 4F
	CAMECA NanoSIMS 50
Primary ion beam and primary ion beam accelerating energy	
	10kV
	O2+, 15 keV
	O2+, 15 keV
	O2+, 15keV
	0-, 12keV
	O2+, 15kV
	<10 namp,
	O2+, 12.5 keV
	O2+, 12.5kV (8.0keV impact)
	O-, 16 keV
Secondary ion extraction kV	
	4.5kV
	4,5 keV
	5 kV
	7
	+5kV
	4.5kV
	about 4.5 kV
	4.5 keV
	4.5kV
	8 kV
Mass resolution used	
	>300
	300
	300
	300
	Mass resolution power (M/deltaM) = 3000
	450
	About 300
	~1000 mass resolving power
	300
	~ 3500 mass resolving power

Secondary ion energy window	
	Not known
	20 eV
	50 eV
	75 eV
	50 eV
	50 eV
	X
	Not measured, but slits wide open
	200V
	Not measured, wide open
EM detector type	
	Balzers SEV217
	on discrete dynodes
	EM made of Cu/Be dynodes
	ETP; Multidynode electron multiplier
	Discrete dynode EM (ETP)
	ETP
	discrete dynode SEM (ETP)
	ETP AF133H
	ETP AF133H
	Hamamatsu small multiplier
Dead time correction applied?	
	Yes
	Yes
	Yes
	No
	Yes
	Yes
	Yes
	No
	Yes
	No
If 'Yes' report the dead time	
	100 ns
	20 nsec
	39 ns
	33 ns
	40 ns
	about 36 nsec
	170 ns
	170 ns

SIMS: measurement conditions	
Presputter conditions (before microprobe measurements)	
	None
	Raster-500, I=30 nA, t=2 min
	10 seconds
	Raster size =25;Primary ion beam intensity=2.90nA
	30nA focused primary beam rastered over 500 microns during a few seconds
	30s
	Usual conditions gave too large uranium signal due to high background contamination
	None
	~ 80 seconds
	None
Microprobe measurement conditions	
	Defocused beam 150micron field <200nano amps
	I= 1,6 nA
	CA:#2(150um), FA:#1(1800um), Image field: 150um
	Raster size =0;Primary ion beam intensity=2.90nA
	5 nA focused primary beam
	0.5nA, 10um raster
	beam current to give stable signal of 100 - 200kcps on U238;
	50-100 nA primary ion current as necessary to give 100-200 kcps count rate on U238
	0.5 to 1nA focussed
	~ 1 nA O- beam
Spot size (estimated diameter)	
	150 microns
	5 micrometers
	10 micron
	2 micron
	about 5 micron
	2 micron
	Few micron
	30 micron
	~ 10 micron
	100 nm
Raster size (if used)	
	NA
	Not
	50 micron
	0
	10 micron
	10 micron raster
	NA
	NA

	0
	3 micron x 3 micron
Masses cycled & cycle times	
	234U=4sec, 235U=4sec, 236U=4sec, 237Np=2sec, 238U=2sec, 238U+1H=2sec over 11 cycles
	2 min 20 sec
	10 cycles & 15 seconds
	235U:1.12s 238U:1.12s
	234, 235, 236, 238, 239: 12s per cycle
	different for different particles
	234, 235, 236, 238, 239; 8,2,8,2,2 sec, respectively 42 cycles/measurement
	233U (Bkg) 0.2 s, 234U 4 s, 235U 5 s, 236U 5 s, 238U 1 s, 239U 0.5 s
	238(2sec), 238+H (5sec),236 (5sec), 235 (6sec), 234 (5sec), 233 (2sec), 10 cycles
	234U 2 s, 235u 2 s, 238u 1 s
Total sputter time per measurement	
	198 s
	45 s
	150 s
	120 s
	about 5 minutes
	se above
	About 20 minutes
	~ 500 s
	380 s
	300 s
SIMS	
238U signal level from particle at start (cps)	
	10E4<cps<10E5
	it depends on particle size
	30000
	100000
	500,000 cps
	different for different particles
	100kcps - 200kcps
	~200,000 cps
	~ 1e5
	~ 10,000-20,000 cps
238U signal level from particle at end (cps)	
	10E4<cps<10E5
	it depends on particle size
	15000
	5000
	150,000 cps

	again not a fixed value
	80kcps - 150 kcps
	~50,000 -100,000 cps
	~ 1e5 but a few dropped to 5e4
	~10,000-20,000 cps
Comment on stability of signal levels during microprobe: stable, decreasing, increasing, variable?	
	linear, mixture of stable, decreasing and increasing count rate vs time
	variable
	decreasing
	decreasing
	Regularly decreasing
	poor stability due to clusters of particles
	generally increasing or decreasing by less than a factor of two over the run; this is much more stable than a typical
	decreasing
	Typically stable. A few particles decreased by a factor of 2
	stable
Comments on appearance of U ion image field (if possible): clear particles?, diffuse spots?, uniform signal? Did this change during the analysis?	
	Clear particles
	it depends on particle size
	Nothing
	diffuse spots, It changed
	Diffuse spots that seemed to spread during the course of the analysis
	The sample has uranium particles in a heavy uranium background of fine or dissolved materials. Due to problems with the web based reporting in inserting data for several particles only a weighted mean for 5 particles is reported
	There were many diffuse bright spots, the more distinctive of which were particles and the others of which appeared to be aggregates of microparticles that gave a less stable signal, although a standard integration on a random spot on the planchet gave the same isotopic results as a
	Appearance of U layer - some variations in intensity, which may be due to topology or denser deposition of particles.
	Clear particles when illuminated by the microprobe on as supplied planchet. Well seperated clear particles on transferred Planchet. Particles are a little more diffuse after analysis
	Clear particles

TIMS: parameters	
Type of TIMS used (brand, model,..)	
	MAT262 and Triton
	Thermo scientific, TRITON
	VG 54 from VG Instruments
Detector used (brand)	
	c) Discrete dynode SEM, d) Ion counting detector operation mode, e) multiple detectors used, f) Single detector used
	d) Ion counting detector operation mode, f) Single detector used
	d) Ion counting detector operation mode, f) Single detector used
Dead time correction applied?	
	Yes
	No
	Yes
If ‘Yes’ report the dead time:	
	Set within software default parameters used
	13ns
Any other correction to the detector output?	
	Yes
	No
	No
If ‘Yes’ please specify:	
	Only that within the software
Specify filament type used	
	a) Single filament technique, c) Zone refined Re
	b) Double filament technique, c) Zone refined Re
	V-shaped zone refined rhenium filament
TIMS	
Measurement of single/multiple particles?	
	Single particles
	Single particles
	Single particles
238U average signal level	
	100000cps or higher
	9352 cps
	from 10000cps to 70000cps (it depends on the particle)
Overall ionisation efficiency (estimate)	
	depending in instrument 0.25% MAT262, 1% Triton
	-0.99999%
	we have no idea of the ionisation efficiency on particles

LA-ICP-MS: parameters	
Type of carrier gas used? (He (%), Ar (%), other)	
	Ar (100%)
	He mixed with 50% Ar after ablation cell
	Ar100% in laser cell
Combination with nebulizer?	
	No
	Yes
	Yes
If 'Yes' please specify type of nebulizer	
	pfa micronebulizer with pfa spray chamber and desolvation unit
	mcn6000
LA carrier introduced into nebulizer or additional mixing of nebulizer?	
	no additional nebulizer
	additional mixing
	additional mixing but a confusing question
Gas flow after LA cell	
	1.025 L/min
	1.7 l/min
	0.7l/min
Type of laser:	
	UV laser (213 nm), New-Wave Inc.
	193 nm ns Nd:YAG laser
	New Wave solid state LUV 266nm
Laser wavelength (nm)	
	213
	193
	266
Energy flux (J/cm2)	
	0.02
	0.1
	0.2 approximately, quite low
Spot size (micrometer)	
	1 and 8 microns
	5 - 15
	35-100
Repetition rate (Hz)	
	5
	10
	2
Ablation type (single spot, line scan, other…)	
	single spot
	single spot
	raster

Type of instrument	
	ICP-SF-MS (single coll., sector field, using low resolution (<1000))
	MC-ICP-MS (multi collector)
	MC-ICP-MS (multi collector)
Type of detector used for each isotope (SEM, channeltron, Faraday cup)	
	SEM
	FC (major isotopes) + IC (minor isotopes)
	faraday for 238, 235, 234; SEM for 234, 236;

Annex 10: Certified reference materials used by the NUSIMEP-6 participants

ID	CRMs and suppliers
1749	U005a, U010, U050 and CRM129-A
1750	NBS U0002, U005a, U010, U050, U500 and U930
1751	Several kinds of materials. Khlopin Radium institute; IAEA - QC samples
1752	NBL U500, U350, U015, IRMM 184
1753	CRM U0002, CRM U015, CRM U350, CRM 130, CRM 111-A, SRM 947 by NBL, IRMM 184
1754	NBL CRM U015 and U350
1755	CRMU005, CRMU200,etc. (NBL)
1756	Liquid standards NBS U500, IRMM 184, IRMM 183
1757	NIST SRMs U-010, U-020, U-030, U-500
1758	mainly the NBSxxx series
1759	NBS U010, U030, U005 from NBL, Monodispersed particles from ITU, NUS1 from Harwell
1766	Nist and IRMM Geel
1767	For this analysis, CRM 129a (primary) and CRM125a (secondary) from NBL.
1768	NBS NIST standards supplied by AWE Aldermaston
1770	IAEA series (IAEA)
1772	Varies
1830	isotopic and elemental matrices; NIST, IRMM
1850	CRM950a, CRM960, CRM112, CRM 115, NBS U010, and we will be doing IRMM ones soon
2110	CRM 129a
2111	NBL and IRMM CRM's are used.

Annex 11: Summary of lab scores

	$n(^{234}U)/n(^{238}U)$		$n(^{235}U)/n(^{238}U)$		$n(^{236}U)/n(^{238}U)$	
Lab_ID	z	zeta	z	zeta	z	zeta
1749			1.93	0.45		
1750	-0.01	-0.01	0.23	0.23	1.38	0.90
1751	3.29	9.93	2.22	29.90		
1752	0.23	0.06	0.80	0.59		
1753	-0.97	-0.52	0.51	0.36		
1754	1.00	0.51	0.80	0.39		
1755			2.07	0.54		
1756			-0.20	-0.06		
1757	0.03	0.05	0.77	1.04		
1758	0.35	0.98	0.17	0.83	1.38	0.51
1759	0.03	0.03	-0.34	-0.48		
1766	331192.24	16499.00	836.98	29.48	130644.63	4.25
1767			-0.06	-0.16		
1768	1.00	1.00	-0.01	-0.04		
1770						
1772	0.68	0.84	-17.66	-1.13	533.96	1.39
1830	-0.25	-0.32	-2.61	-1.08		
1850	-0.13	-0.06	0.62	9.09	-1.62	-3.45
2110			0.51	1.44		
2111	-0.01	-0.31	-0.10	-2.99	-0.85	-22.01

European Commission

EUR 23702 EN – Joint Research Centre – Institute for Reference Materials and Measurements
Title: NUSIMEP-6: Uranium isotope amount ratios in uranium particles
Authors: Yetunde Aregbe, Jan Truyens, Ruth Kips, Stephan Richter, Elzbieta Stefaniak, Heinz Kühn, Monia Kraiem
Luxembourg: Office for Official Publications of the European Communities
2008 – 62 pp. – 21.0 x 29.7 cm
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 978-92-79-08378-5
DOI 10.2787/18380

Abstract
The Additional Protocol (AP) authorizes safeguards authorities to verify the absence of undeclared nuclear activities in all parts of a state's nuclear fuel cycle as well as any other location where nuclear material is or may be present. As part of the Additional Protocol, environmental sampling has become an important tool for the detection of non-declared nuclear activities. In environmental sampling micrometer-sized uranium particles with an isotopic composition characteristic for the processes at the inspected facility need to be collected, identified and analysed. Considering the potential consequences of the analyses, these measurements need to be subjected to a rigorous quality management system.

NUSIMEP-6 focused on measurements of *Uranium isotope amount ratios in uranium particles* aiming to support laboratories involved in uranium particle analysis. It was the first NUSIMEP on particle analysis coordinated by IRMM and was also intended as a pilot interlaboratory comparison in this field to gather feedback towards future optimisation and improvements. NUSIMEP-6 was open for participation to all laboratories in the field of particle analysis, particularly also to the IAEA network of analytical laboratories for environmental sampling (NWAL).

The NUSIMEP test samples were prepared by controlled hydrolysis of well certified uranium hexafluoride close to natural uranium isotopic composition. Participating laboratories in NUSIMEP-6 received a test sample of uranium particles on a graphite planchet with undisclosed isotope amount ratio values $n(^{234}U)/n(^{238}U)$, $n(^{235}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$. The uranium isotope amount ratios were to be measured using their routine analytical procedures. Measurement of the major ratio $n(^{235}U)/n(^{238}U)$ was obligatory; measurements of the minor ratios $n(^{234}U)/n(^{238}U)$ and $n(^{236}U)/n(^{238}U)$ were optional.

15 institutes reported measurement results using different analytical methods, among those 7 NWAL laboratories. The participants' measurement results were evaluated against the certified reference values. In addition, zeta scores were calculated.

The results of NUSIMEP-6 confirm the capability of laboratories in measuring the ratio $n(^{235}U)/n(^{238}U)$ and $n(^{234}U)/n(^{238}U)$ in uranium particles. Difficulties were particularly observed for the ratio $n(^{236}U)/n(^{238}U)$. In addition feedback from the participants was collected in view of improvements and optimisation of future NUSIMEP interlaboratory comparisons for uranium isotope amount ratios in uranium particles.

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LA-NA-23702-EN-C

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ISBN 978-92-79-08378-5
9 789279 083785